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Journal of Chromatography A, 876 (2000) 37–50

JOURNAL OF CHROMATOGRAPHY A

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Analysis of linear and cyclic oligomers in polyamide-6 without sample preparation by liquid chromatography using the sandwich injection method
I. Injection procedure and column stability

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Received 7 June 1999; received in revised form 30 December 1999; accepted 10 January 2000

Abstract

We report a method for reliable routine polymer sample introduction with minimal bias, a separation method of the first six linear and cyclic oligomers by liquid chromatography, quantification using group equivalents and long term method performance. Injecting a polymer sample in a mobile phase containing an aqueous non-solvent often results in blocked systems as the polymer precipitates in the connecting capillaries. In this first part we focus on a new injection technique, in which the dissolved polyamide is placed between two zones of formic acid, preventing the polymer to precipitate before it reaches the column. Development of this sandwich injection method makes direct injection of the polymer into an aqueous acetonitrile gradient feasible. The oligomeric polyamide recovery of this technique, extraction, dissolution/precipitation and direct injection on a hexafluoro–isopropanol (HFIP) gradient were compared. With the sandwich injection method the polymer remains on the column, slowly changing the stationary phase. The influence of this on resolution and retention was studied. Column stability allows sixty injections before cleaning or replacing the column is necessary.

Keywords: Sample introduction; Sandwich injection; Injection methods; Polyamide; Nylon; Polymer

1. Introduction

Polyamide 6 (PA-6), also known as nylon-6, is a polycondensate of caprolactam. PA-6 has achieved the widest commercial use of all the nylons produced and together with nylon-6,6 it is the most commonly used polyamide, finding broad application in the areas of textiles, floor coverings and engineering plastics [1,2].

During the manufacture of nylon-6, the quantities of cyclic and linear monomers and oligomers (Fig. 1) are important parameters in production management and process control. The residual trace amounts of the oligomers present in nylon-6 can have a major impact on the properties of the final polymer. Although usually only a few percent of the oligomers are linear, they are of importance for the physical

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0021-9673/00/$ – see front matter
PII: S0021-9673(00)00179-5

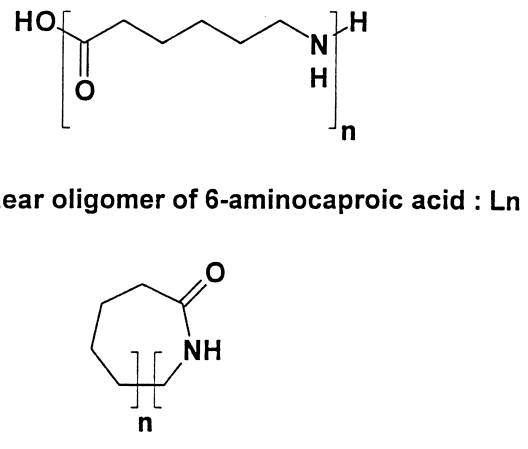

Fig. 1. The chemical structures of the linear and cyclic oligomers of nylon-6.

properties and the investigation of the polymerization mechanism of the polyamide [3–5].

Analysis methods for the separation of the nylon-6 oligomers have evolved through the years. The cyclic oligomers were first determined by the use of fractional sublimation in 1956, followed by paper chromatography a few years later [6,7]. In 1970, Mori reduced the cyclic oligoamides to cyclic oligoamines, so analysis by gas chromatography became feasible [8]. At the same time gel permeation chromatography (GPC) was developed, where with the use of fluorinated modifiers the molar mass distribution of the polymer could be analyzed [9–14]. In addition to this, polymers were extracted to determine the different cyclic oligomers [15–18] and Mori et. al derivatized the extract to determine the linear oligomers [19].

Next, normal and reversed-phase high-performance liquid chromatography became available, with superior selectivities with regard to the oligomers [4,20–27]. Polymers are hard to handle on reversed-phase liquid chromatographic systems. Monomers and oligomers often elute at aqueous conditions where the polymer precipitates instantaneously. Because of this, often only extracted polyamide samples were investigated. This time consuming procedure is satisfactory when determining extractable amounts or the migration of oligomers into a specific matrix [4,25–27], but it is inadequate to determine the true amount of oligomers in the polyamide material.

Although separations of the linear oligomers were performed with thin layer chromatography (TLC) and GPC, as reviewed [5], no straightforward quantitative method for the determination of the cyclic as well as the linear oligomers has been published. In this paper a method for routine use is described, in which the first six cyclic and linear oligomers in a polyamide-6 matrix were separated and determined simultaneously.

When injecting a polyamide sample dissolved in formic acid in a reversed-phase high-performance liquid chromatography (RP-HPLC) system, the mobile phase acts as a precipitant for the polymer, which results in a plugged system. Precipitation and concomitant plugging can be prevented by direct sandwich injection of the dissolved polymer on the column and no further sample preparation is necessary. The solution containing polymer is sandwiched between two zones of formic acid, preventing the polymer from precipitating in the surrounding aqueous mobile phase. The separation of the various cyclic and linear oligomers takes only 33 min, including column equilibration for the next injection [28].

The new method with sandwich injection was compared with the more traditional intermittent extraction and with off-line precipitation of the polymer, all followed by an aqueous acidified water to acetonitrile gradient and with direct injection in an aqueous acidified water to 1,1,1,3,3,3-hexafluoro-isopropanol (HFIP) gradient. This fluorinated alcohol is a good solvent for nylon-6 [9–14], but for routine use the absence of fluorinated solvents like trifluoroethanol (TFE) or (HFIP) is preferable with respect to UV transparency, price and safety [29].

2. Experimental

All polyamides used were synthesized at DSM. Cyclic and linear oligomers are obtained by preparative (HPLC) experiments. The linear oligomers are abbreviated by L*n*, the cyclic oligomers by C*n*, where *n* is the number of $COC_5H_{10}NH$ units. The cyclic oligomers are pure, but the linear oligomers are 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.

The dissolution of the polyamides in formic acid (98–100% p.a., Merck, Darmstadt, Germany) was performed in a Bransonic Ultrasonic cleaner Model 5210 (Danburry, Connecticut, USA).

The sandwich injection method was developed on an HP1090 DR5 solvent delivery system equipped with an autosampler with a 25 μl syringe and a diode array detector (DAD), all from Hewlett-Packard (Waldbronn, Germany) and controlled by a PASCAL workstation. For routine analysis a HP1050 quaternary pump and an HP1050 variable injector with an extended capacity of 115 vials (Hewlett-Packard, Waldbronn, Germany) was used. The aqueous (MilliQ, Waters, Milford, MA, USA) mobile phase A contains 1% acetonitrile (Lichrosolve, gradient grade, Merck, Darmstadt, Germany) and 10 m*M* phosphoric acid (made with phosphoric acid 85%, p.a. Baker, Deventer, The Netherlands) and mobile phase B was pure acetonitrile. With a programmed gradient the pump changed the percentage mobile phase B from 0 to 50 in 22 min with a flow-rate of 1.2 ml/min. The pressure drop (ΔP) along the 250×4 mm Nucleosil 120-5C_{18} column (Machery-Nagel, Düren, Germany) was approximately 200 atm. UV-detection at λ=200 nm was performed with a Linear 204 programmable dual wavelength detector (Linear Instruments, Reno, Nevada, USA). Capillaries to connect the injector device with the column where as short as possible and had an internal diameter of 0.25 mm. Post column reagents were prepared as follows: 50 g boric acid (p.a., Merck, Darmstadt, Germany) was dissolved in 1 l MilliQ water by adding potassium hydroxide pellets (p.a., Merck, Darmstadt, Germany), until a pH of 10 was reached. Next, 0.8 g of *o*-phthalic dicarboxaldehyde (OPA, p.a., Acros Chemica, Geel, Belgium) was dissolved in 10 ml ethanol (Lichrosolve, gradient grade for liquid chromatography, Merck, Darmstadt, Germany) and together with 1 ml 3-mercaptopropionic acid (Fluka Chemika, Buchs, Switzerland) the solutions were added to the borate buffer solution. The post-column flow obtained with a Gilson 302 pump with 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 fluorescence signal was generated with a Waters 474 fluorescence detector (Waters, Milford, MA, USA, 16 μl detector cell, λ_{ex}=330 nm, λ_{em}=420 nm., excitation and emission bandwidth 18 nm). The UV and fluorescence detector signals were collected with a X-Chrom/Windows NT 3.51 version 2.11b data management system (LAB-systems, Manchester, U.K.).

All experiments with 1,1,1,3,3,3-hexafluoro-isopropanol (HFIP) were carried out in a fume hood on a HP1090 PV5 solvent delivery system equipped with an autosampler with a 25 μl syringe and a diode array detector (DAD) all from Hewlett-Packard (Waldbronn, Germany) and controlled with a Windows95 workstation LC-3D version A.05.04. Mobile phase A contained 10 m*M* phosphoric acid in MilliQ water and mobile phase B was pure 1,1,1,3,3,3-hexafluoro-isopropanol (Chemosynthia, Ingelmunster, Belgium). During the gradient the pump changed the percentage mobile phase B from 10 to 90 in 80 min at a flow-rate of 0.2 ml/min. The programmed injection volume was 2 μl and the pressure drop along the 125×2.1 mm Nucleosil 120-5C_{18} column (Machery-Nagel, Düren, Germany) was approximately 100 atm. HFIP was purified by double distillation.

Intermittent extractions were performed on a homemade extraction device. The water (MilliQ) and the methanol (Biosolve b.v., Valkenswaard, The Netherlands) were intermittently heated for 3 min and cooled during 1 min. The original particles (8 mm I.D.) were cryogenically ground to obtain 0.1 mm particles. All experiments were performed in duplicate.

To precipitate the polymer off-line the total sample is prepared in a volumetric flask followed by separation of the oligomers from the polymer by centrifugation of the 60% formic acid and 40% water mixtures for 60 min at 6000 r.p.m. (Labofuga 6000, Heraeus-Christ, Osterode, Germany) or by filtration with a Dynagard 0.2 μm PP syringe filter (Spectrum Microgon, Laguna Hills, CA, USA). The speed of precipitation of the polymer is hard to control, yet it is likely that poor mixing of the non-solvent with the solute could influence recovery. As the cloud point of polyamide 6 is just above 60% formic acid in water, a 100% formic acid/polyamide solute was slowly diluted under continuous vortex mixing with water until the precipitation conditions at 40% water

were reached. Some samples, which were not cloudy within a day, were cooled down to 0°C to increase precipitation. After the filtration or centrifugation of the precipitated mixtures, the solutions stood for another day as post-precipitation could occur, which makes repetition of the filtration or centrifugation necessary

The obtained polymer-free solutions were analyzed using the acetonitrile gradient.

3. Results

3.1. Sample introduction

Extraction or dissolution/precipitation is generally used for the analysis of oligomers in polyamides to provide adequate sample preparation. However, direct injection of the polymer in an RP-HPLC system would decrease sample preparation time and is therefore economically attractive and, moreover, may leave less opportunity for biased results.

In RP-HPLC some polyamide oligomers do elute in mobile phase conditions which are classified as so-called non-solvents for the polyamide polymer, like pure acetonitrile or a mixture of aqueous 0.01 *M* phosphoric acid and 1% acetonitrile. When a polyamide is injected in such a mobile phase, it precipitates and blocks the injector or the connecting capillaries. To avoid blocking at the inlet of the column a special flow distributor was proposed [30]. In our experience the special flow distributor is inadequate to solve the sample introduction problem. It does of course not prevent the polymer from precipitating before reaching the column.

With the sandwich injection method this precipitation can be avoided and therefore a direct polymer injection is possible. The principle of this injection procedure is given in Fig. 2. As formic acid is a good solvent for polyamide, 2 μl of formic acid is aspired into a by-passed injection needle. Directly after this step, 6 μl sample in formic acid and finally again 2 μl of formic acid is aspired in the needle. The polyamide solute is sandwiched between two formic acid zones, preventing precipitation of the polymer in the injector or the connecting capillaries. Precipitation does not take place before the polyamide reaches the column. At the top of the column the

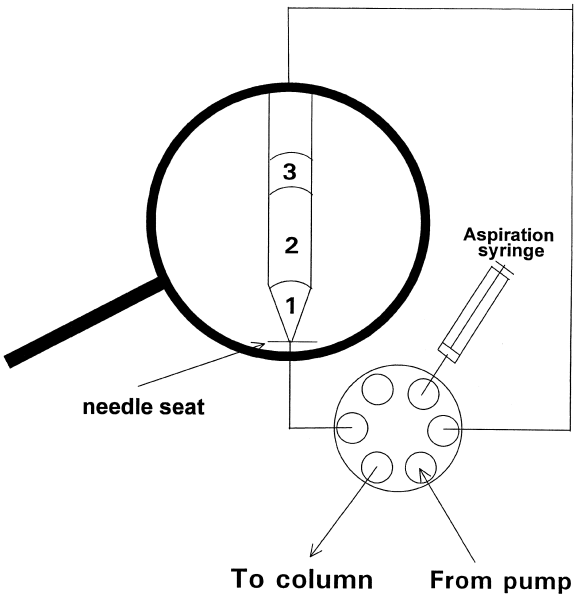

Fig. 2. Schematic view of the sandwich injection principle. Zone one and zone three: each 2 μl formic acid, zone two: 6 μl polyamide-6 sample dissolved in formic acid.

geometry and the large surface to volume ratio cause almost instant precipitation [30].

This sandwich injection procedure can only be performed on a suitable injection device, by which the sample is not transferred through injector tubing, but can be stacked in the needle straight away. After by-passing the injector, the needle moves up from its seat, and the formic acid and solute vials are one after another transported, as programmed, to the needle, which aspirates the established volumes from these vials. At the end of this sub-program, the needle moves back to the injector seat, the injector valve is turned to the inject position and the stacked zones in the needle are swept to the column by the mobile phase. Evidently with the injector used here, the two 2 μl formic acid zones are large enough to prevent the polymer to precipitate before entering the column and the total volume of 10 μl formic acid is small enough to not induce unwanted extra column band broadening and to maintain a uniform pH in the post column reactor, as the response of the first eluting component 6-aminocaproic acid is constant yet decreases when larger zones are used.

In Fig. 3 the dependence on injected mass is given by varying concentrations at fixed injection volumes.

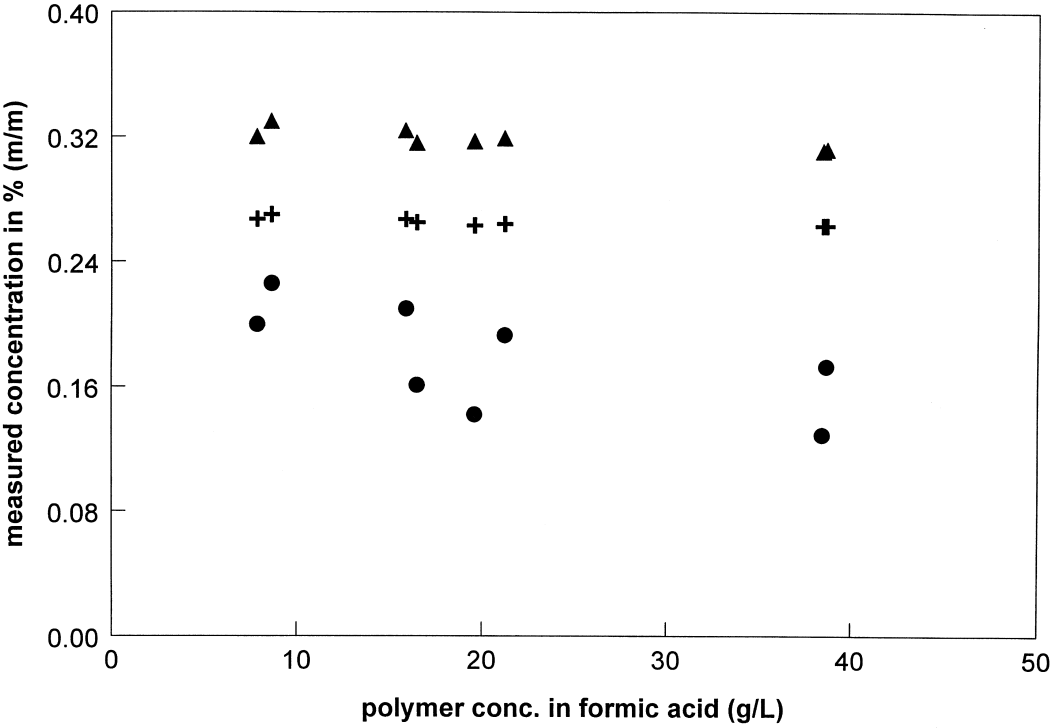

Fig. 3. Dependence of recovery of the cyclic oligomers on the polymer concentration in the sample. (+): cyclic pentamer, (▲): cyclic hexamer and (●): cyclic nonamer.

Approximately 200 mg of polymer dissolves in 10 ml formic acid within an hour by ultrasonic agitation. Up to the cyclic heptamer, no mass dependence is observed. For the cyclic nonamer on the other hand a mass dependence and a reproducibility problem could be observed. In routine use we prefer to work with a 20 g l^{-1} nylon-6 solution in formic acid, but for the first six cyclic oligomers there is no mass-loss found up to 40 g l^{-1} polyamide, although it takes longer to dissolve those amounts and the polyamide–formic acid mixtures are not so easy to handle, as they become viscous. Full recovery was observed with standard additions of 2.5–40 g polymer to a fixed concentration of 750 mg l^{-1} cyclic or linear oligomers in formic acid and with standard additions of 75–1250 mg cyclic or linear oligomers to a fixed concentration of 20 g polymer l^{-1} (in formic acid, data not shown here).

Inasmuch as the polyamide does not elute with the acetonitrile gradient, because this mobile phase acts as a non-solvent, the higher oligomers ($n>6$) remain partially on the column, eluting again partially during the next run and many consecutive runs. These partial eluted oligomers ($n=7$–appr. 20) can be effectively removed from the column by injecting an extra 50 μl formic acid plug at the end of the gradient. Again, not all commercially available autosamplers are capable to perform such an injection, as software often does not allow injecting twice during one chromatographic run.

The injection procedure described above is given in Table 1.

By not utilizing the extra injection plug, it is very

Table 1
Procedure of the sandwich injection method

Time (min)	Action
0	Draw 2 μl formic acid into needle
0	Draw 6 μl sample into needle
0	Draw 2 μl formic acid into needle
0.01	Inject and start gradient time-program
23	Inject 50 μl formic acid onto column

easy to study recovery of the polyamide oligomers qualitatively. All the oligomers, which elute in the next run of a blank formic acid injection, are not completely recovered in the previous run. Fig. 4A and B demonstrates this. It gives some typical chromatograms of a polyamide sample in which, for illustrative purpose, a known amount of linear oligomers has been added. The first not fully recovered cyclic oligomer is the heptamer.

To validate the whole method, the results of the sandwich injection method using an acetonitrile gradient for HPLC separation were compared with three other methods.

Because of the solubility of nylon-6 in HFIP it is essentially better to use HFIP instead of acetonitrile. However, HFIP is not attractive as a routine mobile phase modifier (price/performance) [29]. Nevertheless it can serve as a comparative tool in research investigations.

In Fig. 5, three representative polyamide samples are compared. With the HFIP and acetonitrile gradient the recovery of the oligomers up till the cyclic heptamer is the same, as there are no significant differences measured in the summated total amount of the first six cyclic oligomers. Higher oligomers are recovered to a higher degree with the HFIP gradient, i.e. the total summated amounts of the first nine cyclic oligomers of all three polyamides with the HFIP gradient minus that with the acetonitrile gradients start to deviate from zero. This cumulative recovery deficit is defined as:

$$\sum_{i=1}^{n} = C_{\mathrm{HFIP}} - C_{\mathrm{sandwich}}$$

This deviation is in good agreement with the results of Fig. 4. Although Fig. 4 indicates full recovery of all linear oligomers, this is hard to prove with most real samples as they contain only low concentrations of these oligomers. With two standard addition samples we could prove that the first six linear oligomers are also fully recovered, as can be seen in Table 2.

Besides with the direct injection and HFIP gradient, our method was compared with two off-line methods for the pre-separation of the polyamide and its oligomers. As far as practicality is concerned the two easiest and commonly used alternatives are extraction and off-line dissolution and precipitation of the polymer. As the linear oligomers are only present at very low levels in the polyamide samples, only the content of the cyclic oligomers is compared here.

Extraction with water [Ref. [20] conditions not given and Ref. [23] temperature 90°C 6 h] or with methanol [Ref. [4] conditions not given, Ref. [24] reflux 1 h] are the most widely used methods to pre-separate the oligomers from the polymer. As extraction experiments are time consuming, it is an inconvenient way to determine the real (and not the extracted) amount of oligomers in the polymer samples. Another problem with extraction is the bad solubility of the higher oligomers, which is even worse when the temperature of the liquid decreases to ambient after the extraction. Therefore the whole extracted sample should be analyzed. Although the higher extraction temperature could influence sample stability, polyamide oligomers are inert till at least 100°C and the nylon-6 itself is stable even above 200°C.

To duplicate and compare different extracts made of polyamide samples, extraction efficiencies have to be determined. Fig. 6 shows the extraction recovery with water and methanol, both with 8 and 0.1 mm particles. The samples were analyzed using the acetonitrile gradient. It is rather surprising that extraction with water or methanol are the most widely used methods to pre-separate the oligomers from the polymer as only the cyclic monomer, dimer and trimer are extracted effectively. A specification of the particle diameter is often not given, but Fig. 7 shows clearly that this is an important parameter. It is without doubt that the smaller the particles are, the better is the extraction efficiency. Extraction is of course the best choice if the migration of the oligo amides in certain food simulating matrices have to be studied [26,27,31].

Dissolution/precipitation is a method infrequently used to pre-separate the oligomers from the polymer. Begley et al. [30] used methylene chloride and HFIP to dissolve and methanol to precipitate, but checked the recovery only with the cyclic monomer caprolactam, in spite of the fact that the recoveries of the higher oligomers are more critical.

However, dissolution/precipitation is an easier and better method to use than extraction. With the

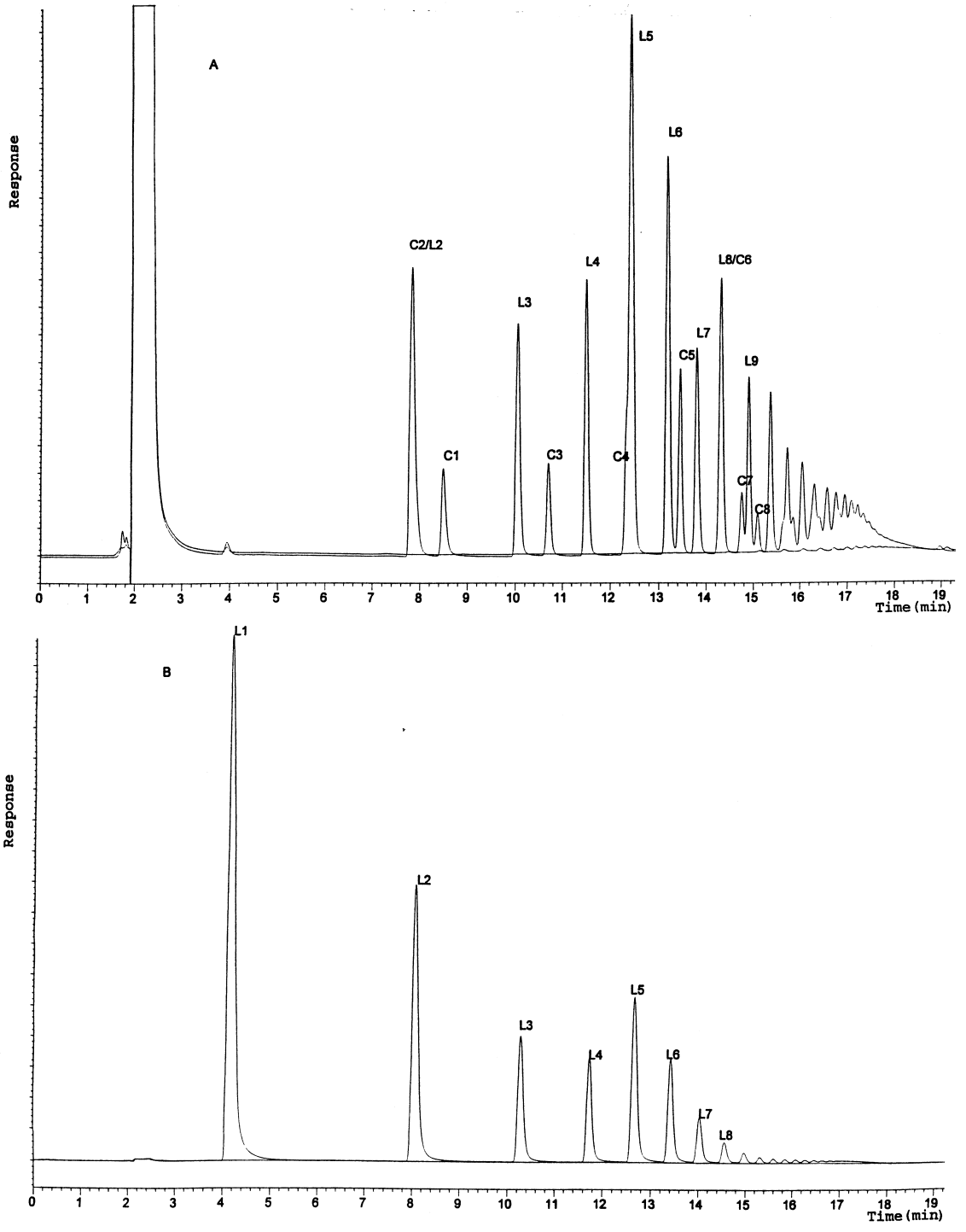

Fig. 4. Influence of a non-50 μl formic-acid plug injection at the end of the chromatographic run at a relatively high acetonitrile concentration. (A) UV-chromatogram ($\lambda = 200$ nm) of a polyamide sample with linear oligomers added and a subsequent blank injection both without the 50 μl formic-acid plug (B) selective fluorescence detection of the post-column derivatized linear oligomers from the same chromatographic runs. Gradient: 1 to 50.5% acetonitrile in 22 min, aqueous phase: 10 m*M* H_3PO_4 in water, flow 1.2 ml/min.

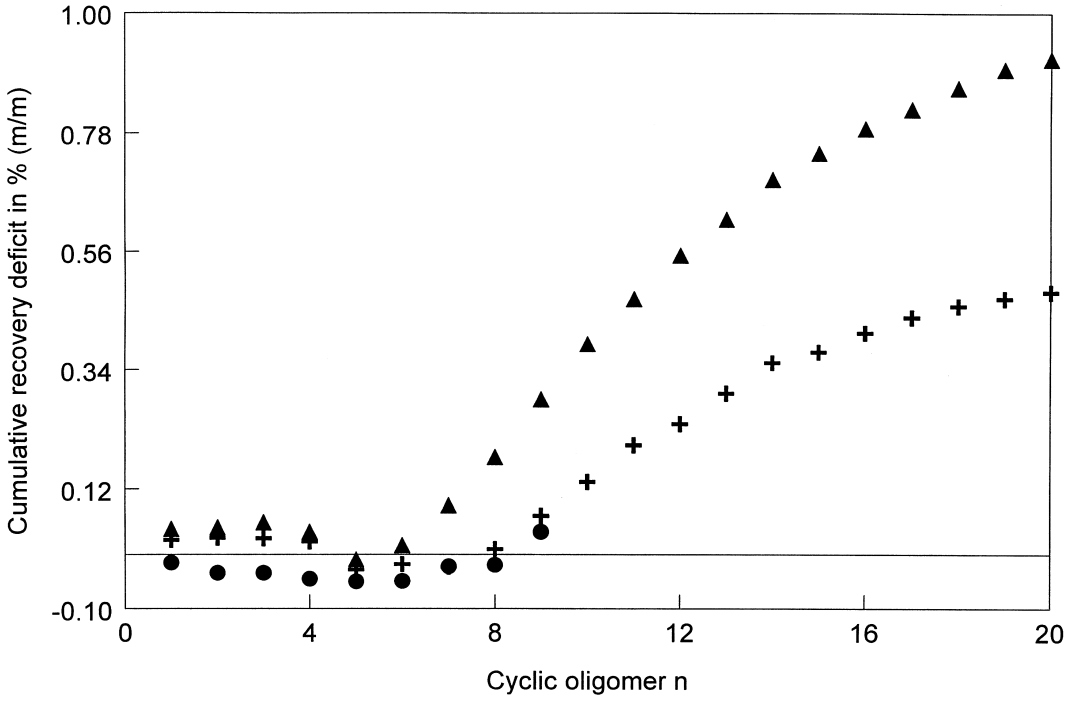

Fig. 5. Summated difference of recovery between the hexafluoro-isopropanol system and the sandwich injection method of three (+, ▲, ●) representative polyamide samples expressed as the cumulative recovery deficit. Initial concentration of oligomers with HFIP gradient: 0.1%C1, 0.04%C2, 0.2%C3, 0.2%C4, 0.3%C5, 0.3%C6% in (m/m).

acetonitrile gradient, there was no dependence of the initial polymer mass observed in the given range for the first eight cyclic oligomers. In Table 3 the results of these precipitation experiments are compared with the sandwich injection and the HFIP method. With eight experiments performed (mass range 40–200 mg polyamide/l), no differences are observed for the first six or seven cyclic oligomers compared to the sandwich injection method and the HFIP gradient. Dissolution/precipitation is an alternative for the

Table 2
Recovery of the linear oligomers in a synthetic sample containing a high concentration of linear oligomers

Linear oligomer	Added amounts of linear oligomers in mg with 20 g polymer/l	Average recover with HFIP method in % (m/m)	Average recovery with sandwich injection method in % (m/m)
1	112.1 and 150.8	[a]	96
2	68.6 and 92.0	100	100
3	42.6 and 56.9	100	102
4	41.5 and 55.0	99	103
5	92.9 and 123.8	101	100
6	70.0 and 90.4	102	98

[a] With the HFIP gradient and the UV detector the 6-ACA is hard to determine as it elutes just after the formic acid peak.

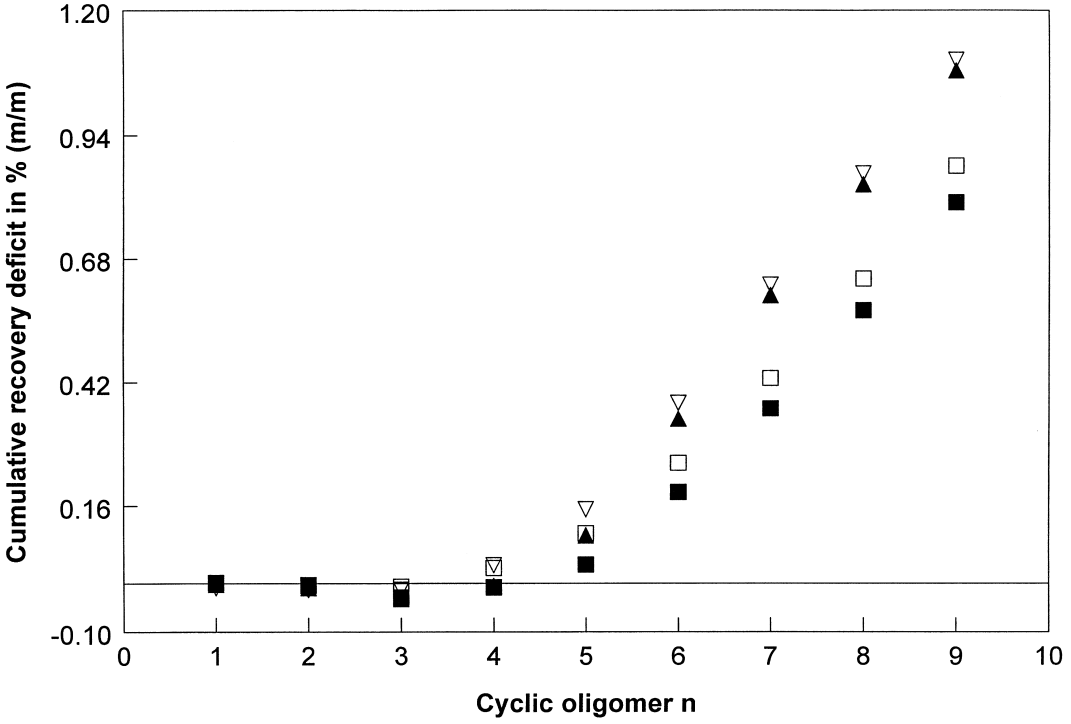

Fig. 6. Relative extraction efficiency of the oligomers with methanol (filled marker) or water (blank) and 8 mm diameter particle (triangle) or 0.1 mm particle diameter (square) expressed as the cumulative deficit relative to the HFIP gradient.

sandwich injection method although it is time consuming.

3.2. Column stability

With each polymer injection 100 μg polyamide and volumes of 10 and 50 μl pure formic acid enter the column. This demands good chromatographic interpretation of the chromatogram. When only polyamide oligomers are injected with the sandwich injection method given in Table 1, a slight shift of the retention times during the first 50–60 injections is observed, after which stable retention times are obtained (Fig. 8a). The resolution of the most critical pair (the cyclic monomer and the cyclic dimer) shows the same trend, as it drops from 4.0 to 2.75 within the first 60 oligomer injections and stays above 2.5 during the next 60 injections, although it is still slightly decreasing (Fig. 9).

When instead of an oligomeric mixture a real nylon-6 polymer is injected, retention time shifts are the same as with the oligomer mixture (Fig. 8b), indicating a slight irreversible modification of the stationary phase. Resolution, however, decreases much faster. After 60 polymer injections it is reduced from 4.0 to 1.0 (Fig. 9). In routine use we replace the column, but in Fig. 9 it is demonstrated that the resolution after the first sixty polymer injections does not decrease at the same rate anymore.

Instead of replacing the column, it can be cleaned by removing the polyamide with 15 ml of HFIP, which constitutes a trade-off in price (column $150, 15 ml HFIP: approximately $30), time and safety.

It is clear that the presence of polymer on the column particles creates secondary adsorption. In Fig. 10 the elution of the cyclic oligomers of nylon-6 is shown after 150 polymer injections and after a subsequent backflush of the column with 15 ml HFIP. The resolution of the cyclic monomer and the

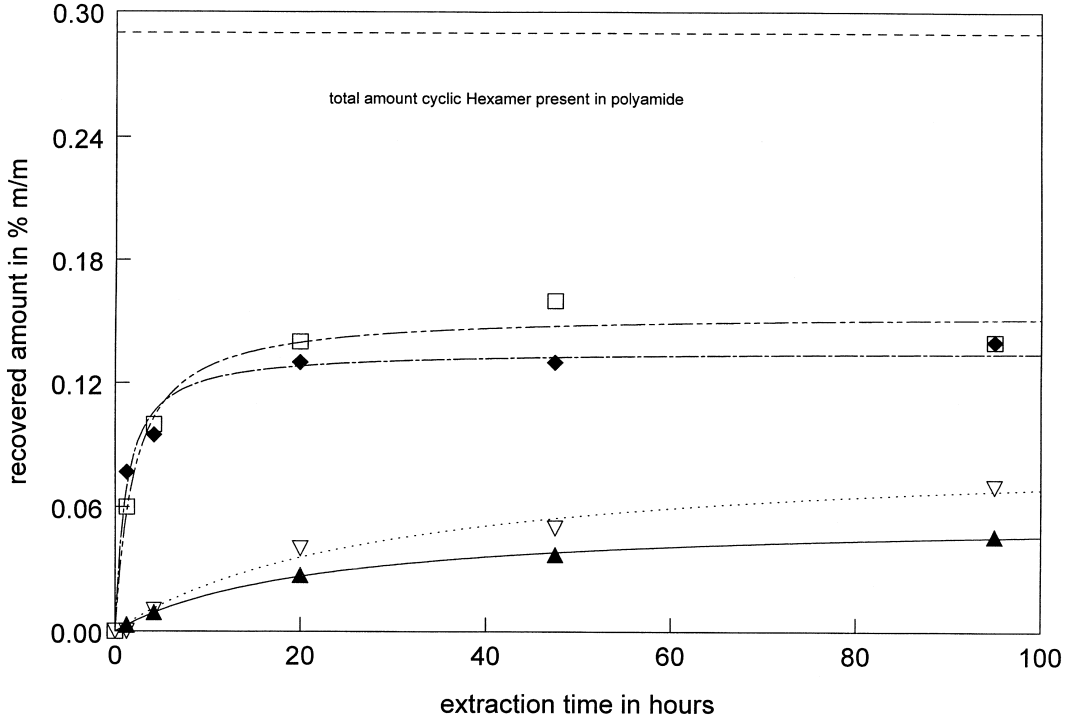

Fig. 7. Extraction efficiency for the cyclic hexamer with methanol (filled marker, dp=8 mm triangle, ———; and dp=0.1 mm square, –·–·–) or water (blank marker, dp=8 mm triangle, · · · · ·; and dp=0.1 mm square, –··–··–) (— — — hexamer content found with HFIP gradient).

Table 3
Determination of the cyclic oligomers in nylon-6 with different sample preparation techniques

Sample preparation	Sandwich injection	Normal injection	Dissolution in formic acid precipitation with water centrifugation	Dissolution in formic acid precipitation with water filtration
Gradient → Cyclic Oligomer	Acetonitrile % (m/m)	HFIP % (m/m)	Acetonitrile % (m/m)	Acetonitrile % (m/m)
1	0.13	0.11	0.13	0.13
2	0.06	0.04	0.06	0.06
3	0.17	0.14	0.17	0.18
4	0.22	0.21	0.23	0.23
5	0.27	0.26	0.27	0.27
6	0.32	0.29	0.33	0.32
7	0.25	0.28	0.31	0.30
8	0.24	0.24	0.18	0.14
9	0.18	0.24	0.12	0.11

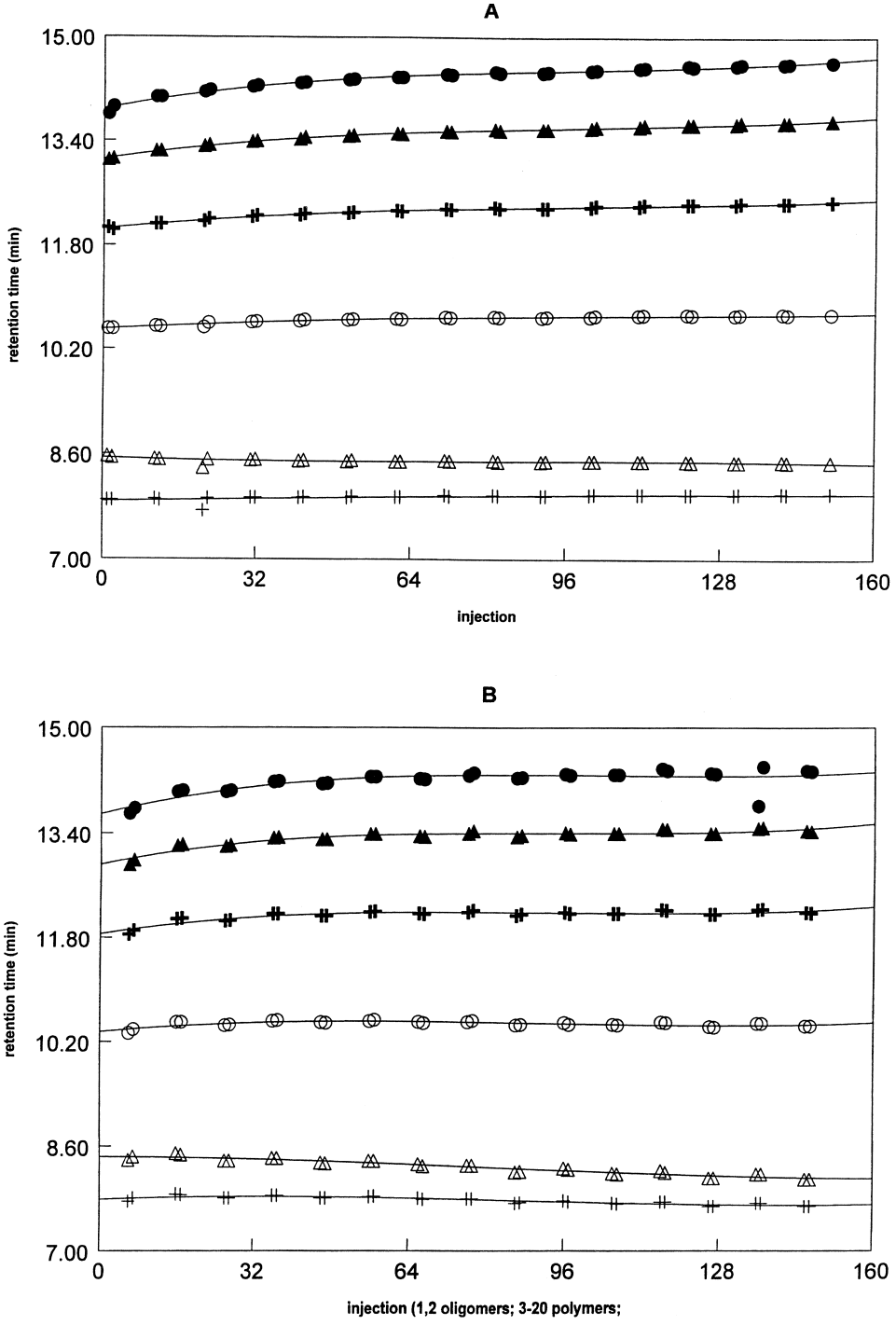

Fig. 8. Retention time stability of the cyclic oligomers, without polymer injected on the column (A) and with polymer injection on the column (B). (+): cyclic dimer, (△): cyclic monomer caprolactam, (○): cyclic trimer, (+): cyclic tetramer, (▲): cyclic pentamer and (●): cyclic hexamer.

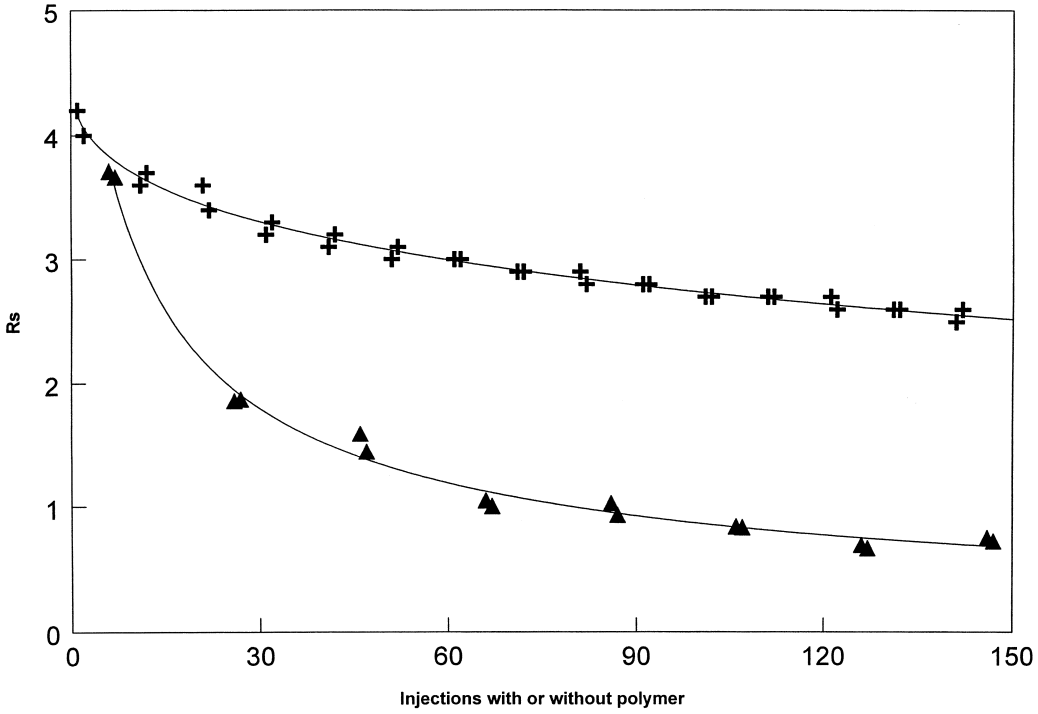

Fig. 9. Resolution between cyclic monomer caprolactam and its cyclic dimer with (▲) and without (+) polymer injection on the column.

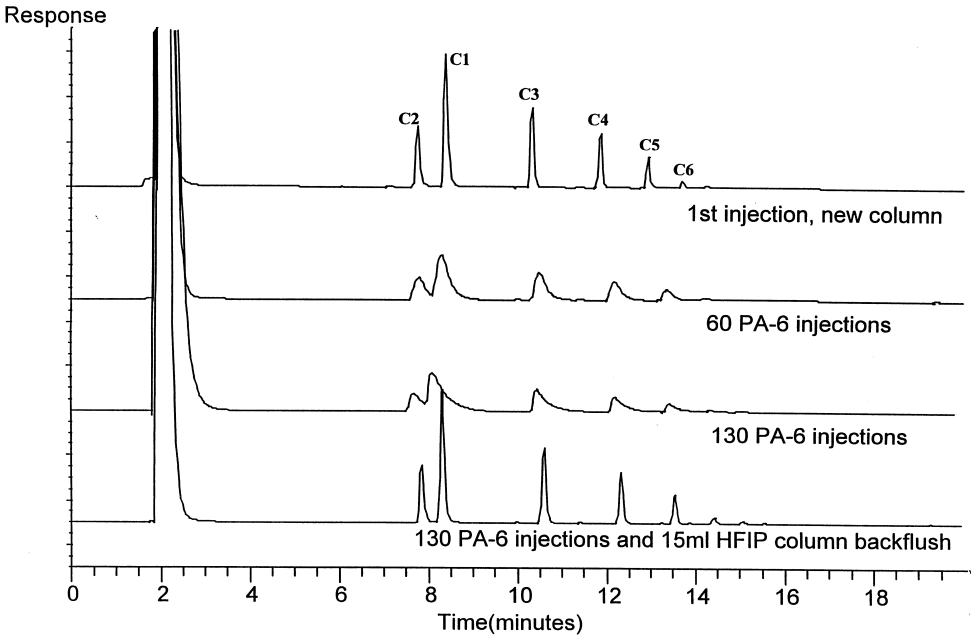

Fig. 10. Chromatograms of cyclic oligomers. (A) First injection on a new column, (B) an injection of an oligomeric mixture after 60 polymer injections, (C) an injection of an oligomeric mixture after 130 polymer injections and (D) an oligomeric mixture after 130 polymer injections and subsequent backflush of the column with 15 ml hexafluoro-isopropanol. Injection 5 μl sample, sandwiched between twice 2 μl of formic acid. Injection of 50 μl formic acid at 23 min.

cyclic dimer returns to 2.75, which is approximately the same resolution which was obtained after the injections of 150 non-polymer containing oligomer samples. This indicates that the modification of the stationary phase by the polyamide is reversible.

4. Discussion and conclusions

It can be anticipated that the sandwich injection method as applied here is applicable in many systems where analysis of monomers, oligomers, additives or compatibilizers in a polymer matrix is necessary. Usually the lower molecular weight components of a polymer mixture are more soluble in common organic solvents, which thus can be used for chromatography, and chromatography method development as well as routine use will be greatly facilitated.

The sandwich injection method is an accurate, reliable and convenient way to determine the first six cyclic and linear oligomers in nylon-6. With an acetonitrile gradient, the recovery of these linear and cyclic oligomers is the same as with an HFIP gradient. The more labor-intensive method of dissolution and precipitation of the polymer gives the same results with respect to cyclic oligomer recovery. Intermittent extraction with methanol or water does not give complete recovery, as only the cyclic monomer, dimer and trimer are fully recovered. By duplicating the time consuming extraction method the particle diameter and the total extraction time were shown to be important parameters, as they influence the extraction efficiency.

With a straightforward acetonitrile gradient the cyclic oligomers are well separated, although the separation between the cyclic monomer and dimer is just sufficient, as on octadecyl modified silica the cyclic dimer elutes directly before its monomer. After approximately 60 injections of 5 μl (60×100 μg polyamide-6 is on the column) the resolution of this critical separation approaches 1, indicating that the column has to be cleaned or replaced.

Acknowledgements

We would like to thank Prof. Dr. Ir. C.A. Cramers and Dr. H.A. Claessens of the Technical University Eindhoven for helpful discussions.

References

[1] Aharoni, n-Nylons: Their Synthesis, Structure, and Properties, John Wiley & Sons, 1997.
[2] Jain, N.D. Sharma, Man-Made Text. India 40 (1997) 245–254.
[3] H.K. Reimschissel, J. Polym. Sci. Macromol. Rev. 12 (1977) 65.
[4] C. Guaita, Makromol. Chem. 185 (1984) 459–465.
[5] R. Puffr, V. Kubanek, in: Lactam-Based Polyamides, Vol. 1, CRC Press, 1990.
[6] Heikens, Recl. Trv. Chim. Pays-Bas 75 (1956) 1199.
[7] Rothe, Makromol. Chem. 35 (1960) 183.
[8] S. Mori, M. Furusawa, T. Takeuchi, Anal. Chem. 42 (1970) 661–662.
[9] S. Mori, Y. Nishimura, J. Liq. Chromatogr. 16 (1993) 3359–3370.
[10] H. Schorn, R. Kosfeld, M. Hess, J. Chromatogr. 282 (1983) 579–587.
[11] E.E. Drott, Liquid chromatography of polymers and related materials, in: J. Cazes (Ed.), Chromatographic Science Series, Vol. 8, Dekker, New York, 1977, pp. 41–51.
[12] A. Moroni, T. Havard, Polym. Mater. Sci. Eng. 77 (1997) 14–16.
[13] W.W. Yau, J.J. Kirkland, D.D. Bly, A Wiley-Interscience publication ISBN 0-471-03387-1
[14] D.J. Goedhart, J.B. Hussem, B.P.M Smeets, Liquid chromatography of polymers and related materials II, in: J. Cazes, X. Delamare (Eds.), Chromatographic Science Series, Vol. 13, New York, 1977, pp. 203–213.
[15] S. Mori, T. Takeuchi, J. Chromatogr. 49 (1970) 230–238.
[16] J.M. Andrews, F.R. Jones, J.A. Semlyen, Polymer 15 (1974) 420–424.
[17] Y. Fujiwara, S.H. Zeronian, J. Appl. Pol. Sc. 23 (1979) 3601–3619.
[18] J.L. Mulder, F.A. Buytenhuis, J. Chromatogr. 51 (1970) 459–477.
[19] S. Mori, T. Takeuchi, J. Chromatogr. 50 (1970) 419–428.
[20] J. Brodilova, J. Rotschova, J. Pospisil, J. Chromatogr. 168 (1979) 530–532.
[21] R. Kulkarni, P. Kanekar, Process Control and Quality 9 (1997) 31–37.
[22] R.N. Nikolov, N.I. Angelova, D.I. Pishev, Khim. Volokna 5 (1992) 57–59.
[23] K. Tai, T. Tagawa, J. Appl Pol. Sc. 27 (1982) 2791–2796.
[24] V. Krajnik, P. Bozek, J. Chromatogr. 240 (1982) 539–542.
[25] C. Guaita, Conv. Ital. Sci. Macromol. 5 (1981) 295–298.
[26] C.T. Barkby, G. Lawson, Food Addit. Contam. 10 (1993) 541–553.
[27] H. Soto-Valdez, J.W. Gramshaw, H.J. Vandenburg, Food Addit. Contam. 14 (1997) 309–318.

[28] M. Vestjens, M. Kerkhoff, Y. Mengerink, J. Hellenbrand, H. Omloo, H. Linssen, Sj. van der Wal, Determination of cyclic and linear oligomers of Nylon-6; Poster presented at HPLC '99, San Francisco.
[29] Y. Mengerink, Sj. van der Wal, H.A. Claessens, C.A. Cramers, J. Chromatogr. A 871 (2000) 259–268.
[30] W.J. Staal, P. Cools, A.M. Herk, A.L. German, Chromatographia 37 (1993) 218–220.
[31] T.H. Begley, M.L. Gay, H.C. Hollifield, Food Addit. Contam. 12 (1995) 671–676.