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# Headspace solid-phase microextraction — a tool for new insights into the long-term thermo-oxidation mechanism of polyamide 6.6

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## Abstract

Low-molecular-mass products formed during thermo-oxidation of polyamide 6.6 at 100°C were extracted by headspace solid-phase microextraction and identified by GC–MS. A total of 18 degradation products of polyamide 6.6 were identified. In addition some low-molecular-mass products originating from the lubricants were detected. The identified degradation products were categorized into four groups where compounds within each group contain the same structural feature. In groups A, B and C several new thermo-oxidation products of polyamide 6.6 were identified including cyclic imides, pyridines and structural fragments from the original polyamide chain. 1-Pentyl-2,5-pyrrolidinedione (pentylsuccinimide) showed the largest increase in abundance during oxidation. The cyclopentanones in group D were already present in the un-aged material. Their amounts decreased during ageing and they are thus not formed during thermo-oxidation of polyamide 6.6 at 100°C. The identified thermo-oxidation products can be formed as a result of extensive oxidation of the hexamethylenediamine unit in the polyamide backbone. The degradation products pattern shows that the long-term thermo-oxidative degradation, just like thermal degradation and photo-oxidation of polyamide 6.6, starts at the *N*-vicinal methylene groups. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Headspace solid-phase microextraction; Thermo-oxidation; Polyamide 6.6

## 1. Introduction

Throughout their lifetime, polymers are subjected to destructive factors such as mechanical stress, chemicals, UV-light and high temperatures. These factors will cause degradation and ultimately affect the performance and lifetime of the polymers. During the last decades, the low-molecular-mass degradation products from polymers have been studied to deduce the various mechanisms of degradation and also to gain a complete knowledge of the environ-

mental impact of the polymers [1–3]. Studies of degradation mechanisms have not only served as a basis for prolonging the lifetime of polymers, but many studies have aimed at enhancing the degradation rate of large volume plastics, such as polyethylene, to overcome the rapidly increasing problems of landfills filling with slowly degrading waste plastic products [4–6]. Most studies have been performed on the large volume plastics, such as polyethylene (PE) and polypropylene (PP), and little attention has been given to the engineering plastics.

Identification of the low-molecular-mass degradation products is a prerequisite in establishing the degradation mechanisms. Prior to identification

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appropriate methods must be developed to separate the low-molecular-mass products from the polymer. Solid-phase microextraction (SPME) is a relatively new extraction technique, first presented in 1990 by Arthur and Pawliszyn [7]. It is based on a fused-silica fibre coated with a polymeric stationary phase. The fibre is introduced directly into aqueous samples or the headspace over the liquid or solid sample matrix. During the extraction the analytes partition between the fibre and the sample matrix according to their partition coefficients. Although the amount of analytes recovered by SPME is relatively small compared to several other methods, there are no analyte losses due to sample handling and the entire extraction is desorbed into the injection port of the gas or liquid chromatograph. Several fibre materials with different polarities are commercially available. The choice of an appropriate stationary phase affects the sensitivity of the method. SPME has earlier been successfully applied to the extraction of, for example, degradation products from low-density polyethylene (LDPE) [8] and toxic compounds from soil [9,10].

Earlier studies of degradation products from polyamide 6.6 have focused on degradation under photo, thermal or pyrolytic conditions [11–19], whereas studies of thermo-oxidation of polyamide 6.6 have focused on changes taking place in the matrix of the material [20,21]. Hence, little attention has been given to the long-term thermo-oxidation degradation products and the mechanisms of their formation. The aim of the present study was to establish the degradation processes taking place during long-term thermo-oxidation of polyamide 6.6 at a relatively low temperature. The low-molecular-mass degradation products were extracted by SPME after different oxidation times and subsequently identified by GC–MS.

## 2. Experimental

### 2.1. Material

Granules of a commercially available unstabilised polyamide 6.6 (Zytel 101L) were generously supplied by DuPont (Stockholm, Sweden). The material was not stabilised against thermal oxidation but

contained some lubricant, probably an aliphatic oil, added to the material to facilitate processing operations.

### 2.2. Extrusion of sheets

A counter-rotating twin-screw extruder DSK 35/9 D from Brabender (Duisburg, Germany) was used to produce sheets from the polyamide granules. The extruder was equipped with an adjustable flat sheet die head (100×0.2 mm) giving 200- $\mu$ m thick polyamide sheets. During the extrusion operation, the three heated zones of the extruder were all set to 285°C. The screw speed was 30 mm/min. The granules were dried for 8 h at 90°C in a Piovan granulate dryer (Venezia, Italy) before extrusion.

### 2.3. Thermo-oxidation

The samples were cut out from the extruded sheets as strips of ~1.5×5 cm in size. Strips weighing 2±0.1 were placed in 20-ml closed headspace vials (Chrompack, Middelburg, The Netherlands) with a PTFE-silicone-rubber septum cap from Perkin-Elmer (Stockholm, Sweden). The vials were placed in a conventional circulating air oven (Heraeus, Hanau, Germany) and the samples were thermo-oxidised for 25, 100, 500 and 1200 h at 100±2°C.

### 2.4. Extraction

Three SPME fibres from Supelco (Bellafonte, CA, USA) were tested for the extraction of polyamide 6.6 degradation products: polydimethylsiloxane-divinylbenzene (PDMS-DVB), Carbowax-divinylbenzene and polyacrylate. PDMS-DVB was found to be superior in extracting the degradation products as it not only extracted more products from the headspace but also generated larger peak areas in the chromatogram than the other phases and thus was chosen for the further studies. The degradation products were extracted on the fibre by subjecting it to the headspace over the films in the vials for 30 min at 80°C.

To compare the relative amounts of degradation products after different oxidation times, an internal standard was added to each sample prior to extraction. By using an internal standard, possible errors in the extraction can be eliminated. The

relative peak areas of the peaks were calculated by dividing the area of the internal standard by the areas of the peaks. The internal standard also serves as an indicator of repeatability in the performance of the SPME fibre. The internal standard used was an ester, methyl-heptanoate, from PolyScience (Niles, IL, USA). An internal standard solution was prepared by diluting 5  $\mu\text{l}$  of the ester with 10 ml of chromatography-grade water, LiChrosolv, from Merck (Darmstadt, Germany). Then 1  $\mu\text{l}$  of the standard solution was added to each vial prior to extraction.

### 2.5. Gas chromatography–mass spectrometry

The gas chromatography–mass spectrometry analyses were performed on a GCQ mass spectrometer from ThermoFinnigan (San José, CA, USA). The column used was a wall-coated open tubular (WCOT) fused-silica low bleed Cp-Sil 8CB from Supelco (30 m $\times$ 0.25 mm I.D, film thickness 0.25  $\mu\text{m}$ ). The column temperature was initially held at 40°C for 3 min. The oven temperature was then increased to 250°C at a heating rate of 10°C/min and then held at 250°C for 10 min. Helium of scientific grade purity from AGA (Stockholm, Sweden) was used as carrier gas with a constant velocity of 40 cm/s. The extracted degradation products were desorbed from the SPME fibre by placing the fibre in the injector of the GC for 5 min at 220°C. The injector was operated in the splitless mode. To identify and quantify the products, MS was run in the EI mode with an electron energy of 70 eV. The detector scanned in the mass-range from 35 to 400  $m/z$  with a scan time of 0.43 s. The temperatures of the ion source and the transfer line were 180 and 275°C, respectively. Some samples were also run in the CI mode using methane as reagent gas to confirm the molecular ions.

### 2.6. Identification of degradation products

The identity of most of the products was confirmed by comparison of the recorded mass spectra of the degradation product to the mass spectra and retention time of an authentic compound run under the same conditions. The latter were generated by exposing the fibre to the headspace over the standard compounds for a short time,  $\sim$ 1 or 2 s, and then

desorbing the extracted compounds into the GC–MS. The same GC–MS method was used for the standard compounds as for the degradation products. The identification was positive if the mass spectrum and retention time of the standard compound was identical to the mass spectrum and retention time of the degradation product.

Not all degradation products could be identified by comparison to authentic compounds since they were not commercially available. These products were identified by comparing their mass spectrums to the mass spectrums included in a reference library, NIST 98, developed at the National Institute of Standards and Technology (Gaithersburg, MD, USA). The identity of some of the compounds could be further confirmed by literature mass spectrums [22–25].

## 3. Results and discussion

Fig. 1 shows the GC–MS chromatograms of the low-molecular-mass products extracted from the polyamide 6.6 after 25 and 1200 h of thermo-oxidation at 100°C. Comparison of Fig. 1a and b clearly shows how the number and quantity of the products increased during the thermo-oxidation. A total of nine degradation products in low amounts were detected after 25 h of oxidation. After 1200 h 14 degradation products were identified and the amount of several products had increased. However, the amount of some of the products had decreased during the ageing and four products that were identified after 25 h of ageing were no longer found after 1200 h of ageing. Low-molecular-mass products were also extracted from un-oxidised polyamide 6.6 to see if some of the products are already present in un-aged samples. These products have been formed for example during processing of the material. In these chromatograms only a few peaks with small peak areas were present. However the actual amounts of low-molecular-mass products in unaged samples might be somewhat higher because it probably takes more than 30 min (the extraction time) for the products to migrate from the core of the material to the headspace where the extraction takes place. Altogether 18 different polyamide degradation products were identified. The names and relative areas of the identified products are given in Table 1.

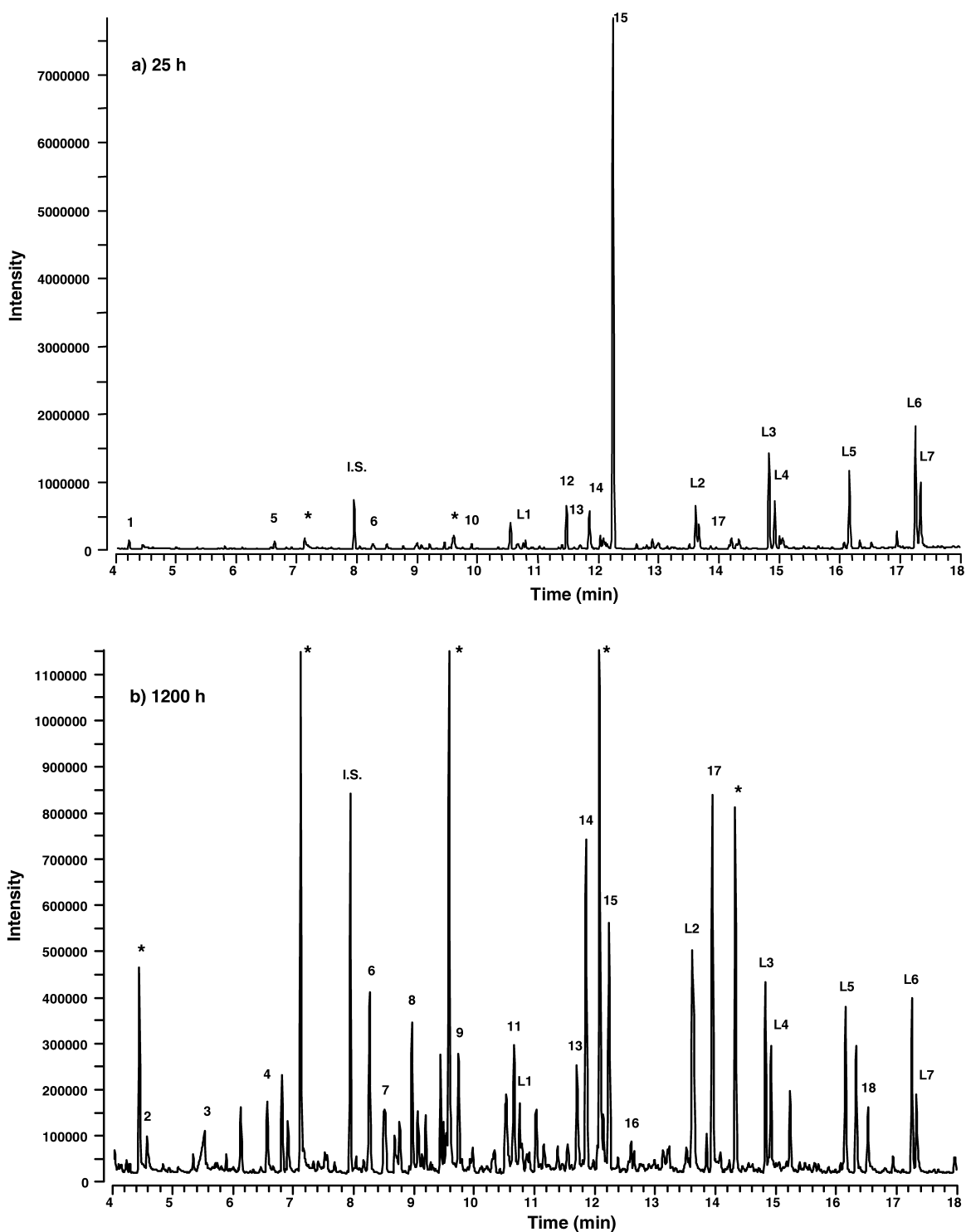


Fig. 1. Ion chromatogram of products evolved after (a) 25 h and (b) 1200 h of ageing in 100°C. Numbered peaks are identified in Tables 1 and 3. I.S., internal standard. \*Peaks corresponding to compounds originating from rubber septum used to seal the vials.

Table 1  
Identified degradation products from thermal oxidation of polyamide 6.6 at 100°C and their relative areas

Peak No.	$t_R$	Compound	Oxidation times (h)			
			25	100	500	1200
1	4.2	Cyclopentanone <sup>a</sup>	19±2	11±1	0	0
2	4.6	2-Methyl-pyridine <sup>b</sup>	0	9±1	9±1	15±1
3	5.5	Pentanoic acid <sup>a</sup>	0	0	0	29±5
4	6.57	Butanamide <sup>a</sup>	0	0	15±2	23±2
5	6.63	2-Ethyl-cyclopentanone <sup>b</sup>	17±3	13±1	0	0
6	8.3	Pentanamide <sup>a</sup>	12±3	37±5	49±6	66±2
7	8.5	3-(1-Methylethyl)-pyridine <sup>b</sup>	0	0	0	37±2
8	9.2	2-Butyl-pyridine <sup>b</sup>	0	0	0	16±1
9	9.7	<i>N,N</i> -hexamethylenebisformamide <sup>b</sup>	0	17±1	23±3	38±4
10	9.9	2-Butyl-cyclopentanone <sup>b</sup>	10±1	8±1	0	0
11	10.6	Glutarimide <sup>a</sup>	0	0	35±8	46±7
12	11.5	2-Pentyl-cyclopentanone <sup>a</sup>	89±6	59±2	9±2	0
13	11.7	Caprolactam <sup>a</sup>	17±3	33±3	25±5	38±3
14	11.8	Azepane-2,7-dione <sup>b</sup>	96±7	149±6	107±18	100±7
15	12.2	2-Cyclopentyl-cyclopentanone <sup>a</sup>	1323±82	1053±38	306±46	82±7
16	12.6	1-Butyl-2,5-pyrrolidinedione <sup>b,c</sup>	0	0	4±1	11±1
17	14.0	1-Pentyl-2,5-pyrrolidinedione <sup>c</sup>	4±2	29±2	63±11	106±8
18	16.5	2-Butyl-3,5-dimethylethyl-pyridine <sup>b</sup>	0	0	85±15	45±10

<sup>a</sup> Identified by comparison with authentic compound.

<sup>b</sup> Identified by comparison with NIST 98.

<sup>c</sup> Identified by comparison with spectrum from literature.

Several peaks, identified as compounds originating from lubricants added to the polymer, also appeared in the chromatograms. The peaks were denominated L<sub>1</sub>–L<sub>7</sub> and are marked accordingly in the chromatograms. The compounds originating from the lubricants were identified as linear alkanes or alkenes with lengths ranging from 10 to 17 carbons. The names and relative amounts of these products are presented in Table 2.

The identified polyamide degradation products were categorized into four different groups according

to Table 3. Each group shares a common structural feature. The products in group A are cyclic imides. The products in group B are pyridine derivatives. In group C all products have structural features that can be deduced from the repeating unit of the polyamide whereas the products in group D are cyclopentanone derivatives.

### 3.1. Group A — cyclic imides

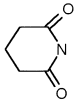
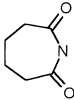
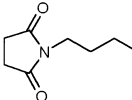
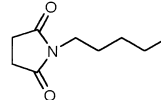

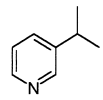
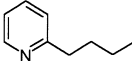
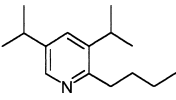
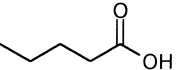
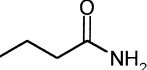
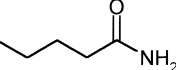
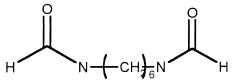
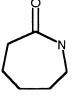

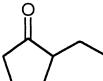
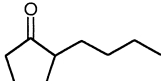
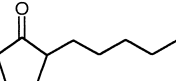
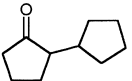
Several cyclic imides, i.e. 2,6-piperidinedione

Table 2  
Names and relative amounts of extracted alkanes and alkenes from lubricant added to polymer

Peak No.	$t_R$	Compound	Oxidation times (h)			
			25	100	500	1200
L <sub>1</sub>	10.8	Dodecane	12±4	30±4	25±6	20±2
L <sub>2</sub>	13.6	Tetradecane	89±17	321±16	129±49	57±5
L <sub>3</sub>	14.8	Pentadecene	178±50	444±23	163±52	46±6
L <sub>4</sub>	14.9	Pentadecane	97±18	190±10	93±30	41±3
L <sub>5</sub>	16.2	Hexadecane	186±25	452±13	152±60	46±6
L <sub>6</sub>	17.2	Heptadecene	271±76	70±20	177±54	44±5
L <sub>7</sub>	17.3	Heptadecane	202±12	263±5	98±31	31±2

All compounds were identified by comparison with authentic compound.

Table 3  
Identified degradation products from polyamide 6.6

<b>Group A: The cyclic imides</b>				
				
2,6-piperidinedione	Azepane-2,7-dione	1-butyl-2,5-pyrrolidinedione	1-pentyl-2,5-pyrrolidinedione	
<b>Group B: The pyridines</b>				
				
2-methyl-pyridine	3-(1-methylethyl)-pyridine	2-butyl-pyridine	2-butyl-3,5-dimethylethylpyridine	
<b>Group C: The chain fragments</b>				
				
Pentanoic acid	Butanamide	Pentanamide	N,N-hexamethylenebisformamide	Caprolactam
<b>Group D: Cyclopentanone and some of its derivatives</b>				
				
Cyclopentanone	2-ethyl-cyclopentanone	2-butyl-cyclopentanone	2-pentyl-cyclopentanone	2-cyclopentyl-cyclopentanone

The products have been divided into four different groups where products sharing a common structural feature belong to the same group.

(glutarimide), azepane-2,7-dione, 1-butyl-2,5-pyrrolidinedione and 1-pentyl-2,5-pyrrolidinedione, were detected after oxidation. As shown in Fig. 2 the amounts of the cyclic imides increased during the

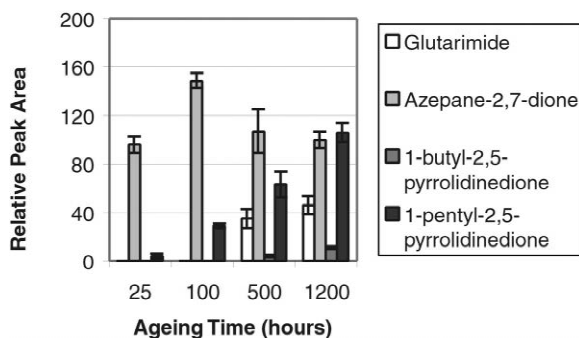


Fig. 2. Relative peak area of the cyclic imides formed during thermal oxidation of polyamide 6.6 at 100°C.

oxidation; 1-pentyl-2,5-pyrrolidinedione especially showed a rapid increase in abundance. At the beginning of oxidation it was only found at trace levels, but after 1200 h its relative peak area had increased to over 25 times the original size, making it the most abundant degradation product.

According to Marek and Lerch [11], succinic acid, dialdehydes and pyrrole are formed due to extensive photo-oxidation and ultimately chain scission of the hexamethylenediamine unit in the polyamide chain as shown in Fig. 3. It has been shown that both photo- and thermo-oxidative degradation of polyamide starts by abstraction of a hydrogen atom from the *N*-vicinal methylene group, according to Fig. 4, so it is expected that succinic acid, dialdehydes and pyrrole are also formed during thermo-oxidation. No dialdehydes or pyrroles were however detected in our study. This is in accordance with earlier studies on thermo-oxidation of PE. After short-term thermo-oxidation of PE at 230°C homologous series of

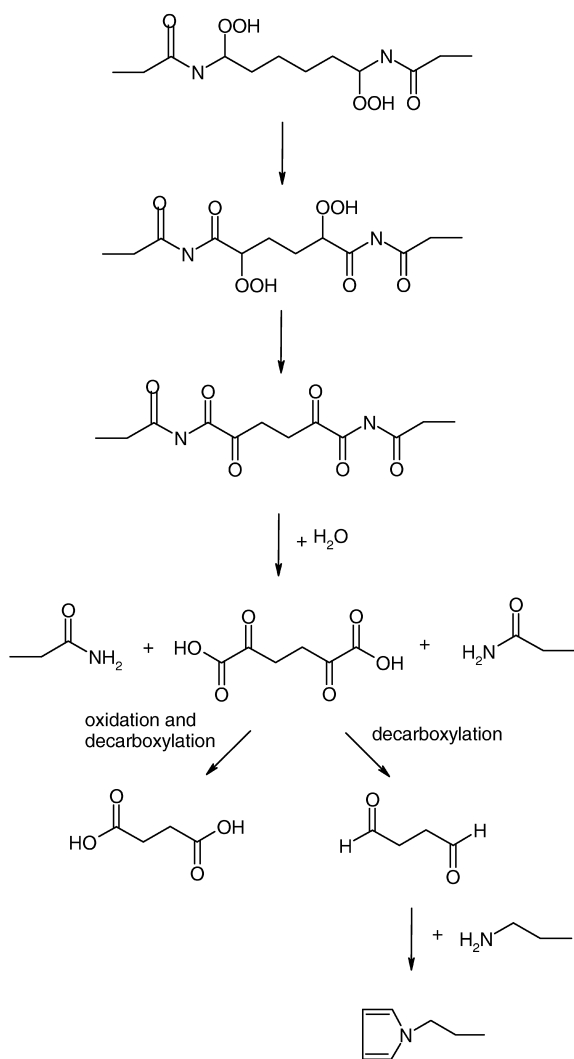


Fig. 3. Formation of dialdehyde, succinic acid and pyrrole as a result of extensive oxidation of polyamide 6.6 according to Marek and Lerch [11].

aldehydes and carboxylic acids were identified [26]. However after long-term thermo-oxidation at 80°C the aldehydes were not detected due to further oxidation to carboxylic acids on prolonged ageing [27]. Dialdehydes may also be formed during the long-term thermo-oxidation of polyamide 6.6 but they are subsequently oxidised to succinic acid. The conversion of dialdehydes to succinic acid also prevents the formation of pyrroles. The identified N-alkylsuccinimides might be formed in an amino-

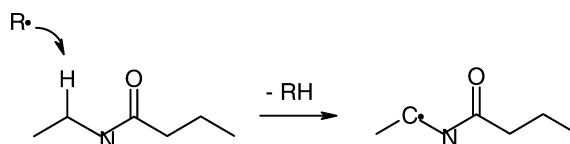


Fig. 4. Initial abstraction of hydrogen from N-vicinal methylene by radical according to Levantovskaya et al. [28].

lysis reaction between the succinic acid and free alkylamines, or a free amino chain end, according to Fig. 5. The formation of azepane-2,7-dione might also start according to the mechanism in Fig. 3. After the hexamethylenediamine unit in the polyamide chain has been fully oxidised and four carbonyl groups have been formed, the polymer backbone is broken generating succinic acid. If this oxidation takes place at two neighbouring hexamethylenediamine units then the adipic acid unit separating them is converted to adipamide. The adipamide can undergo ring-closure, thus producing ammonia and the cyclic imide azepane-2,7-dione. Our findings of rather large amounts of cyclic imides, both substituted as well as un-substituted, as in the case of azepane-2,7-dione, show that multiple oxidation of the aliphatic chain fragment takes place to a large extent in the unstabilised polyamide 6.6.

### 3.2. Group B — pyridine derivatives

The different pyridine derivatives were generally only formed after rather long ageing times. Fig. 6 shows the relative areas of 2-methyl-pyridine, 3-(1-methylethyl)-pyridine, 2-butyl-pyridine and 2-butyl-3,5-dimethylethylpyridine after different ageing times. After 25 h no pyridine derivatives had been formed. The first pyridine derivative, i.e. 2-methyl-pyridine, appeared in the chromatograms after 100 h of oxidation. The amount of 2-methyl-pyridine increased only slightly during the prolonged ageing.

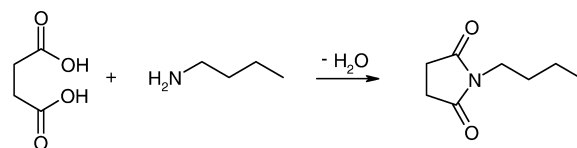


Fig. 5. Formation of N-butylsuccinimide from succinic acid and butylamine.

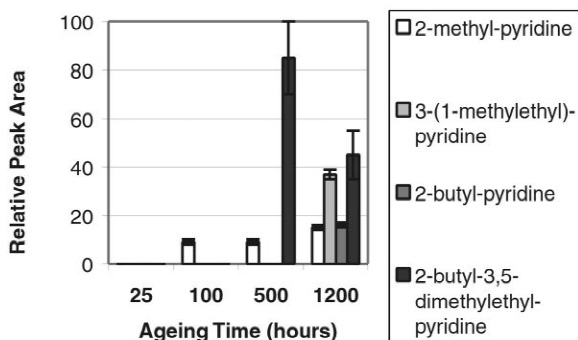


Fig. 6. Relative peak area of the pyridine derivatives formed during thermal oxidation of polyamide 6.6 at 100°C.

After 500 h a large amount of 2-butyl-3,5-dimethylethyl-pyridine had been formed. However, the amount of 2-butyl-3,5-dimethylethyl-pyridine decreased on prolonged ageing, probably due to further degradation of 2-butyl-3,5-dimethylethylpyridine to 3-(1-methylethyl)-pyridine and 2-butyl-pyridine, which appeared in the chromatograms after 1200 h.

### 3.3. Group C — chain fragments

The products in group C all have structural features that can be deduced from the repeating unit of the polyamide 6.6 chain. As shown in Fig. 7 they also show similar behaviour during the oxidation and

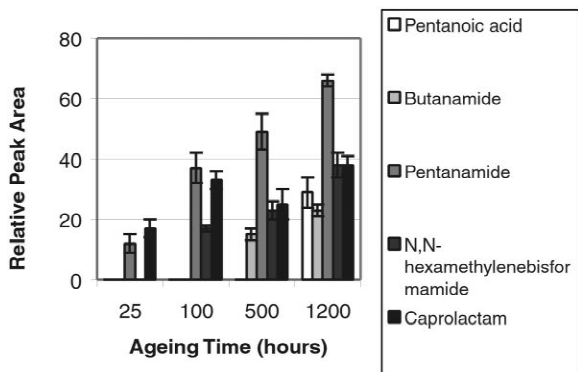


Fig. 7. Relative peak area of some compounds originating from polymer chain during thermal oxidation of polyamide 6.6 at 100°C.

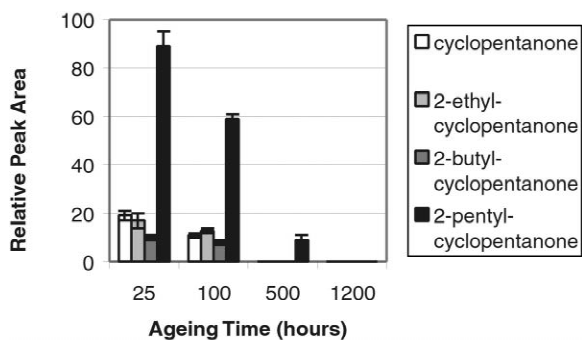


Fig. 8. Relative peak area of cyclopentanone and some of its derivatives as a function of ageing time at 100°C.

the amount of all the products in group C increased with oxidation time. The pentanamide is the most abundant degradation product within group C. It is together with caprolactam detected from the beginning of the oxidation. All the compounds in this group have a carbonyl group at their endpoints. Hence, these products were most likely formed as a result of chain cleavage in the vicinity of the amide group, i.e. the degradation takes place mainly at the *N*-vicinal methyl group.

### 3.4. Group D — cyclopentanone derivatives

Cyclopentanone and four cyclopentanone derivatives were identified: 2-ethyl-cyclopentanone, 2-

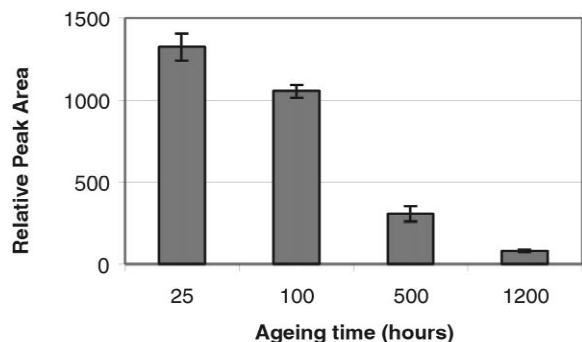


Fig. 9. Relative peak area of 2-cyclopentyl-cyclopentanone as a function of ageing time at 100°C.



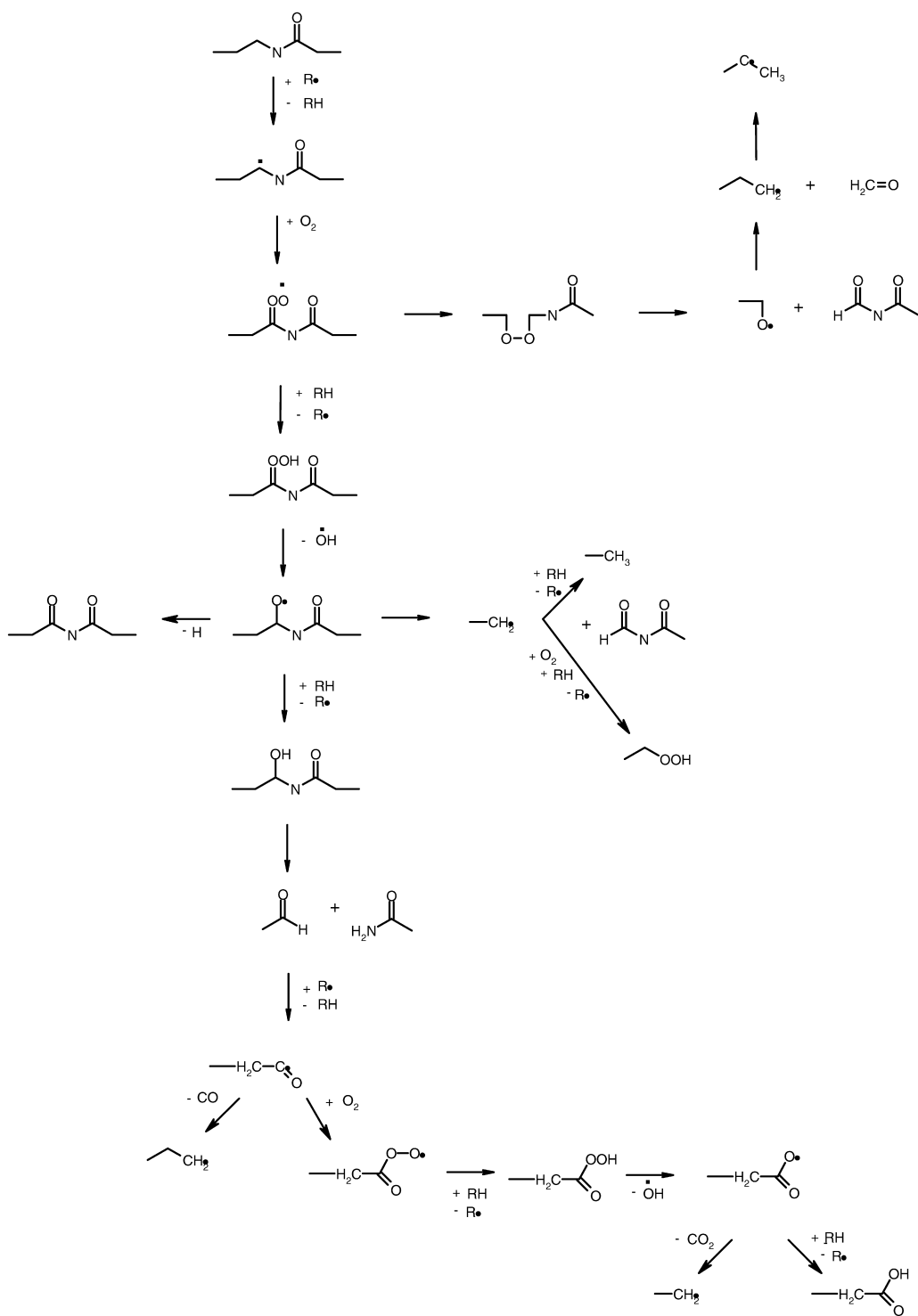


Fig. 10. Oxidation route of polyamide, starting at the N-vicinal methylene group, according to Karstens and Rossbach [20].

butyl-cyclopentanone, 2-pentyl-cyclopentanone and 2-cyclopentyl-cyclopentanone. As seen in Figs. 8 and 9, the amount of all of the cyclopentanones was highest at the beginning of the ageing and decreased on prolonged oxidation. After 25 h of oxidation 2-cyclopentyl-cyclopentanone was the most abundant product in the chromatograms. The other cyclopentanone derivatives were only detected in small amounts. The relative areas of the other cyclopentanones were ~1% of the relative area of the 2-cyclopentyl-cyclopentanone peak. After 1200 h, 2-cyclopentyl-cyclopentanone was the only cyclopentanone derivative detected. Its peak area had however decreased to only 6% of the amount measured after 25 h. This means that the cyclopentanone derivatives were not formed during thermo-oxidation at 100°C, but had already been formed during the production or processing steps.

Cyclopentanone and 2-ethyl-cyclopentanone have earlier been detected after thermal degradation [14] and pyrolysis [15–19] of polyamide 6.6 in an inert atmosphere, i.e. the cyclopentanone derivatives are formed during thermal degradation in the absence of oxygen. Even other cyclopentanone derivatives where the substituent in 2-position is a methyl-, propyl-, butyl-, pentyl-, or hexyl-group, have been identified in pyrolysed samples [19]. The formation of cyclopentanone is believed to proceed through ring-closure of the adipic acid unit in the polymer backbone. Our results support this mechanism, i.e. a reaction that does not involve oxygen. This reaction is also more probable at higher temperatures used for example during processing, when the material is in liquid phase and the ring-closure mechanism can more easily take place.

Earlier thermo- and photo-oxidation studies of polyamide 6.6 have shown that the *N*-vicinal methylene group in the polymer chain is very susceptible to oxidation, i.e. it is in this site in the polymer chain where the oxidation is most likely to start. In 1989, Karstens and Rossbach [20] presented a reaction scheme, which is based on the work by Levantovskaya et al. [28], for the thermal oxidation of polyamide 6.6. This scheme is now generally accepted among several authors [29,30]. According to the mechanism as presented in Fig. 10, the degradation starts with a radical attack at the *N*-vicinal methylene group when a proton is abstracted from the methylene group leaving a radical at the *N*-

vicinal methylene group. This radical may subsequently react with oxygen forming a new peroxy-radical. It may then isomerise or follow one of several possible reaction routes, each resulting in chain-scission and formation of carbonyl and carboxyl end-groups. This sensible initiation site means that the number of products formed during thermo-oxidation of polyamide is considerably lower than the number of products formed during oxidation of, for example, PE, where due to the random degradation mechanism, hundreds of different products can be formed [26,27,31].

#### 4. Conclusions

The sensitive SPME method allowed detection of trace amounts of products after early stages of thermo-oxidation of polyamide 6.6. Altogether 18 degradation products of polyamide 6.6 were identified and to our knowledge most of these products have not been reported earlier as polyamide degradation products. The degradation products were divided into four groups, i.e. cyclic imides, pyridines, cyclopentanones and chain fragments. Chain fragments included for example butyramide and pentanoic acid. After 1200 h at 100°C, 1-pentyl-2,5-pyrrolidinedione was the most abundant degradation product. The *N*-alkyl-substituted succinimides (pyrrolidinediones) might be formed in an aminolysis reaction between succinimide and a free alkylamine or a free amino chain end. Large amounts of cyclopentanone and its derivatives were extracted from the unoxidised polyamide 6.6. The concentration of cyclopentanones decreased during the course of oxidation, which shows that cyclopentanones are not formed during thermo-oxidation at 100°C but they are rather formed as a result of thermal degradation during polymerisation or processing. The degradation product pattern indicates that the thermo-oxidative degradation preferentially starts at the *N*-vicinal methylene group and proceeds throughout the hexamethylenediamine-unit of the polyamide 6.6 chain.

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