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DEGRADATION OF NYLON-6 BY GLYCOLYSIS. PART 1: IDENTIFICATION OF DEGRADATION PRODUCTS

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Key Words: Nylon-6, Polymer Degradation, Depolymerization, Glycolysis, Caprolactam

ABSTRACT

Glycolysis of nylon-6, in the presence of phosphoric acid at 250°C, leads to a mixture of low molecular weight compounds. HPLC analysis combined with ^{1}H-NMR and mass spectroscopy showed that the main degradation products were ethylene glycol derivatives of caprolactam and linear oligomers. No cyclic oligomers were found.

Two types of linear oligomers were found i.e. with free carboxylic acid endgroups and with the carboxylic acid endgroups esterified with ethylene glycol.

INTRODUCTION

Poly(ε-caprolactam), or nylon-6, is an important bulk polymer with an estimated world production of 2.3(10^6 m^3/year [1]. Due to its relatively high price, this poly-mer is a prime candidate for "chemical recycling". Two strategies for chemical recycling can be considered. The first one is the recovery of the monomer through ring-closing depolymerization. This general concept has been discussed by

Höcker [2]. The second possibility is converting high molecular weight polymer into low molecular weight telechelic polymers which can be used as starting material for the synthesis of segmented copolymers.

We have investigated the glycolysis of nylon-6 as a possible way for both strategies. Ethylene glycol is a solvent with high polarity and boiling point (197°C) which dissolves nylon-6 at elevated temperature. Olesiak *et al*. [3] studied the glycolysis process with the aim of synthesizing low molecular weight polymer with -OH and $-NH_2$ endgroups. However, the formation of low molecular weight compounds was not reported.

The purpose of the present research was to study the low and high molecular weight degradation compounds formed during acid-catalyzed glycolysis with the aim of better understanding the mechanism and kinetics of degradation. The present paper focuses on the identification of the degradation products.

EXPERIMENTAL

Materials

Nylon-6 (Akkulon F224) was supplied by DSM (Geleen, The Netherlands) and used as provided. Ethylene glycol, caprolactam, ε-aminocaproic acid, KtBuO, methane sulfonic acid, p-toluenesulfonic acid monohydrate, o-phtalaldehyde (OPA), 3-mercaptopropionic acid, 2-bromoethanol, 3,4-dihydro-2H-pyran, dimethylformamide (DMF) and trifluoroacetic acid anhydride (TFAA) were supplied by Acros. Anhydrous phosphoric acid was supplied by Aldrich. Sodium caprylate was obtained from Fluka. N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) was supplied by Alltech.

Water for HPLC was purified using a Milli-Q Waters purification system. Tetrahydrofuran (THF) and acetonitrile were supplied by Lab-Scan.

Glycolysis of Nylon-6

Ethylene glycol (270 g) and nylon-6 (80 g; 0.707 mol monomer units) were placed in a closed stainless steel titanium-coated reaction vessel. The reactor was heated to 270°C in approximately 45 minutes. Anhydrous phosphoric acid (6.93 g; 0.0707 mol) dissolved in ethylene glycol (50 g, 0.806 mol) was added and the temperature set at 250°C.

Samples were taken at regular times. The polymer was removed by filtration from the reaction mixture after cooling to room temperature. The polymer was washed with hot water (60°C) containing 5g/L KOH, water and finally methanol to

remove residual ethylene glycol and low molecular weight compounds. The residue was dried overnight at 60°C.

Synthesis of Ethylene Glycol Ester of Caprylic Acid

Sodium caprylate (2 g, 0.012 mol) and 2-bromoethanol (1.51g, 0.012 mol) were dissolved in DMF (150 mL). After 3 hours refluxing, DMF was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 and unreacted sodium caprylate was removed by filtration. The glycol ester of caprylic acid was obtained after removing CH_2Cl_2 under reduced pressure.

Synthesis of N-(2-Hydroxyethyl)-caprolactam (HECL)

KtBuO (2.244 g, 0.02 mol) was added to a solution of caprolactam (2.26 g, 0.02 mol) in 40 mL of DMF under stirring at room temperature. 1-Bromo-2-(2'-tetrahydropyranoxy)-ethane (4.18 g, 0.02 mol) dissolved in 10 mL of DMF was added dropwise. After 4 hours, the reaction mixture was cooled to room temperature, the formed KBr was removed by filtration. DMF was evaporated from the filtrate under vacuum and 50 mL of methanol was added. The solution was acidified with p-toluenesulfonic acid. After 3 hours stirring at room temperature the solvent was removed under reduced pressure, 50 mL of water was added and made alkaline with $NaHCO_3$, followed by extraction with CH_2Cl_2 (3(50mL). The combined CH_2Cl_2 fractions were dried ($MgSO_4$) and the solvent removed under reduced pressure. A mixture of caprolactam (20% m/m) and HECL (80% m/m) was obtained. Pure HECL was obtained by preparative HPLC.

Synthesis of 1-Bromo-2-(2'-tetrahydropyranoxy)-ethane

1-Bromo-2-(2'-tetrahydropyranoxy)-ethane was synthesized using a method reported earlier (4(for the synthesis of tetrahydroxypyranylether of 5-bromo-2-pentanol.

HPLC

HPLC of Caprolactam, the Cyclic Oligomers and Derivatives

The HPLC analysis were performed using a Kontron 325 pump equipped with a Kontron 440 UV DAD detector and Hypersil ODS (250 mm L (4.6 mm i.d.) column. Gradient was prepared from aqueous solutions of 5% acetonitrile (solution A) and 40% acetonitrile (solution B), the amount of B being increase from 0 % to 7.5% in 15 minutes, followed by increasing B from 7.5% to 80% in 15 minutes. After 5 minutes at the latter composition, the mixture was restored to 100% A over a period of 5 minutes. The flow rate was 1 mL/min. Samples were injected using a Gilson 234 autoinjector provided with a 20 μL loop.

Preparative HPLC

The same system was used as described above, but equipped with a preparative C18 column (500 mm L (22 mm i.d.). Gradient was prepared from aqueous solutions of 5% acetonitrile (solution A) and 40% acetonitrile (solution B). The amount of B was increased from 0% to 80% in 100 minutes. The flow rate was 5 mL/min.

HPLC of the Linear Oligomers

The HPLC analysis were performed using a Kontron 325 pump equipped with a Kontron 440 UV DAD detector and Hypersil ODS (250 mm L (4.6 mm i.d.) column. Gradient was prepared from aqueous phosphate buffers (0.01 M, pH 3) with 5% acetonitrile (solution A) and 40% acetonitrile (solution B), the amount of B being increase from 0% to 40% in 20 minutes. After 5 minutes at the latter composition, the mixture was restored to 100% A over a period of 5 minutes. The flow rate was 1.2 mL/min. Samples were injected using a Gilson 234 autoinjector with 20 µL loop. After the column, a reaction coil (20 m L (0.2 mm i.d.), thermostated in a water bath (35°C), and a LKB 2150 HPLC pump was mounted to perform the post-column derivatization. The flow of the OPA reagent was 0.5 mL/min.

The OPA reagent was prepared by dissolving 0.8 g of OPA in 10 ml methanol, and mixing this solution with 750 mL degassed aqueous potassium borate buffer (0.4 M: pH 10). 3-Mercapto-propionic acid (1 g) was added. The OPA reagent was kept under nitrogen atmosphere.

^{1}H-NMR

^{1}H-NMR spectra were obtained on a Bruker 360 Mhz spectrometer at room temperature using deuterated chloroform as solvent.

Derivatizations were performed in the NMR tubes. Typically, 100 µL TFAA was added to 20 mg product in 0.6 mL anhydrous deuteroform and mixed until a clear solution was obtained and stored overnight at room temperature before analyzing.

Gel Permeation Chromatography (GPC)

GPC was performed with a Waters 510 HPLC pump with Knauer differential refractometer equipped with PL gel 5 µ mixed-D. THF, distilled over CaH_2 under atmospheric pressure, was used as eluent. Flow rate was 1 mL/min.

Typically, 100 µL of TFAA was added to 20 mg of product dissolved in 1 mL of anhydrous methylene chloride and allowed to react overnight. The suspension turned into a colorless solution. Solvent, excess TFAA and trifluoroacetic acid were removed under reduced pressure to avoid corrosion of the chromatograph by

trifluoroacetic acid. The residue was redissolved in 2 ml of anhydrous THF for analysis.

Calibration was performed against polystyrene standards.

GC-MS

The samples (5 mg) were derivatized with BSTFA (250 μL) at 60°C for 15 minutes. After dilution with CH_2Cl_2, the samples were analyzed on a HP 5890 series II gas chromatograph. The instrument was coupled to a HP 5972 Mass Selective Detector. The GC column was a WCOT-HP-5MS, 30 mL x 0.25 mm i.d. x 0.25 μm film thickness. Helium was used as carrier gas at a flow rate of 0.8 mL min^{-1}. 1 μL was injected on column applying the following temperature conditions: from room temperature to 70°C at 50°C min^{-1}, then to 280°C at 5°C min^{-1}.

Atmospheric Pressure Chemical Ionization Mass Spectroscopy (APCI)

The analysis was performed on a HP1100 series LC/MSD (Hewlett Packard), which was equipped with a dual air-cooled turbomolecular pump vacuum system and incorporates a hinged swing-out spray chamber enabling a fast switching between atmospheric pressure chemical ionization and electrospray modes. A gold-plated RF octapole ion guide was installed prior to the single quadrapole to increase the transmission of ions and reduce ion energy spread. The APCI was utilized for the identification.

RESULTS AND DISCUSSION

The glycolysis of nylon-6 was performed in the presence of phosphoric acid in a high pressure closed reaction vessel at 250°C. At regular times, samples were taken and analyzed. After 10-30 minutes, the reaction products are mainly partly de-graded polymer. As the reaction time increases, larger fractions of low molecular weight compounds are formed. After three hours, no more polymer could be detected.

In the following paragraphs, cyclic degradation products, linear degradation products and low molecular polymers will be discussed.

Monomer, Cyclic Oligomers and Related Compounds

The polymerization of caprolactam is characterized by the simultaneous formation of low molecular weight cyclic species $[NH(CH_2)_5CO]_x$. In the melt at 500 to 550°K, crude nylon-6 contains approximately. 12% (m/m) of cyclic products in equilibrium with the linear polymer [5]. Of this fraction, *ca.* 3-4% (m/m) comprises cyclic oligomers for which $x \geq 2$. This ring-chain equilibrium has been

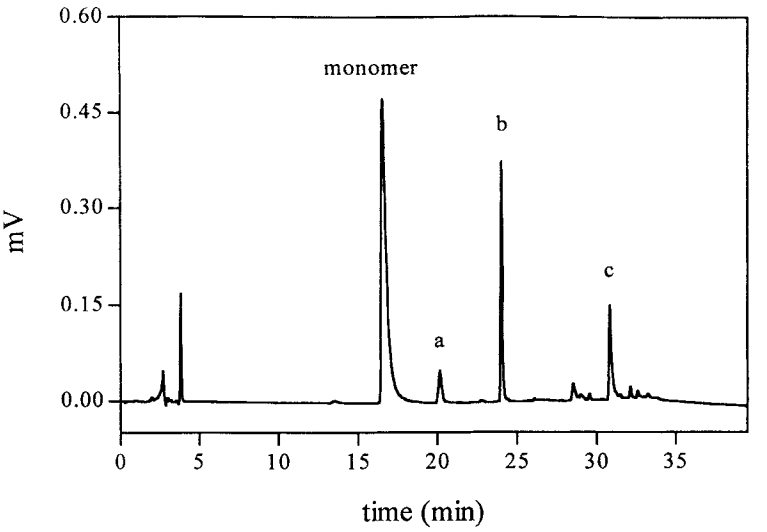


Figure 1. HPLC analysis of the reaction mixture after complete degradation of the polymer (8 hours at 250°C; a = HECL, b = HOPCL , c = EDCL).

theoretically described by Jacobson and Stockmayer [6]. For nylon-6, this equilibrium has been investigated by several authors [5, 7].

A number of reports describe the use of HPLC for the determination of cyclic oligomers of caprolactam using a reversed phase column [8, 9]. A modified method, using different solvent, gradient and column, was developed: separation was performed on a C18-column using a gradient prepared from aqueous solutions of 5% acetonitrile and 40% acetonitrile. The method was tested on a mixture of oligomers isolated from a commercial production mixture of nylon-6 by extraction with water. Figure 1 shows a typical chromatogram which is similar to a chromatogram reported previously [8, 9] indicating that the used analytical technique was reliable.

Figure 2 shows a typical chromatogram of a reaction mixture after glycolysis. Comparing Figures 1 and 2 shows that caprolactam is the only detectable cyclic product, having structure $[NH(CH_2)_5CO]_x$. Although compound b in Figure 2 has an elution time close to that of the cyclic trimer, it was found that this compound is not the cyclic trimer.

Compounds b an c were isolated by preparative HPLC and analyzed by ^{1}H-NMR spectroscopy and mass spectroscopy. Figure 3 shows the ^{1}H-NMR spectrum

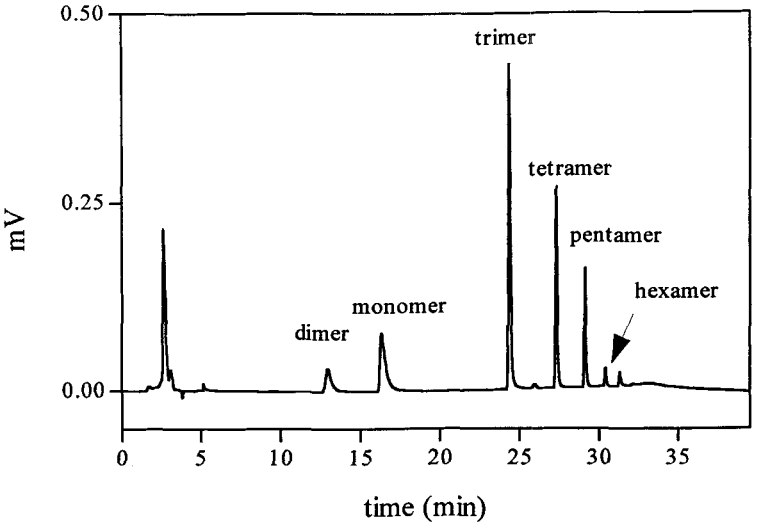


Figure 2. HPLC analysis of a mixture of cyclic oligomers and caprolactam (extract from commercial production mixture).

of b and Figure 4 the spectrum of c. Both are found to be N-substituted derivatives of caprolactam: b is N-(5-hydroxy-3-oxa-pentyl)-caprolactam (HOPCL) and c is N,N'-ethylene-di(caprolactam) (EDCL) (Scheme 1).

It was confirmed that the peak at 2.1 ppm in the ^{1}H-NMR spectrum of HOPCL (Figure 3) corresponds to the proton on the alcohol function (and residual water) because the peak disappears after addition of trifluoroacetic acid anhydride.

Compound a could not be isolated by preparative HPLC. However, the presence of HOPCL in the reaction mixture suggests that N-(2-hydroxyethyl)-caprolactam (HECL) might be formed as an intermediate. Therefore, this compound was synthesized separately and analyzed by HPLC. The elution times for compound a and for synthesized HECL were found to be identical.

Additional proof for the structure of compound a was found by analysis of the reaction mixture by gas chromatography coupled to mass spectrometry (GC-MS). For this purpose, the reaction mixture, as well as HECL were derivatized with N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA). The chromatogram of the reaction mixture showed the presence of a compound having the same elution time and the same mass spectrum as that obtained from HECL.

Consequently, it was concluded that compound a in the chromatogram of Figure 1 is HECL.

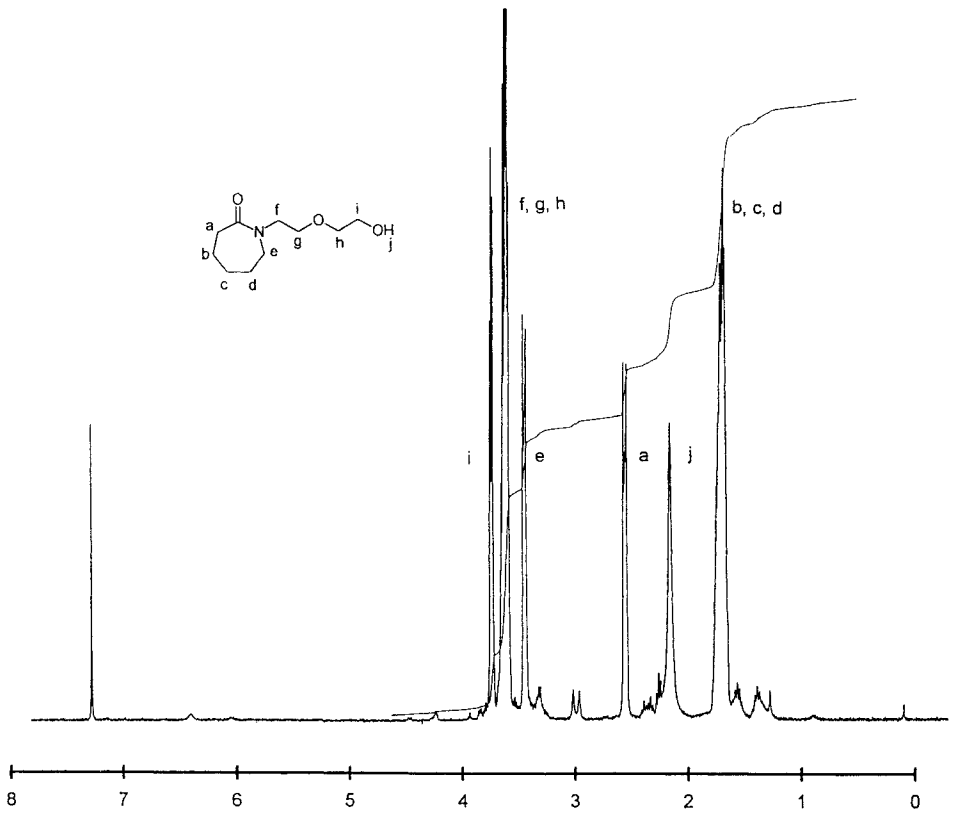


Figure 3. ^{1}H-NMR spectrum of b (HOPCL), isolated from the reaction mixture with preparative HPLC.

Linear Oligomers and Related Compounds

During the commercial production of nylon-6, small amounts of linear species, having structure H-[NH$(CH_2)_5$CO]$_x$-OH, are formed. Mori and Takeuchi [10] used gel permeation chromatography (GPC) to separate and determine these compounds. They found that under the usual reaction conditions for polymerization, only 0.17% (m/m) of linear oligomers (linear monomer included) were present compared to 11-12% (m/m) of cyclic oligomers (caprolactam included). The formation of the linear oligomers was explained by a side reaction, i.e. hydrolysis of the cyclic oligomers during the polymerization or during the work-up process (e.g. extraction).

In the present study, the polymer was degraded in glycol solution. Therefore, we expected the formation of linear species with esterified carboxylic acid functions H-[NH$(CH_2)_5$CO]$_x$-O$(CH_2)_2$-OH.

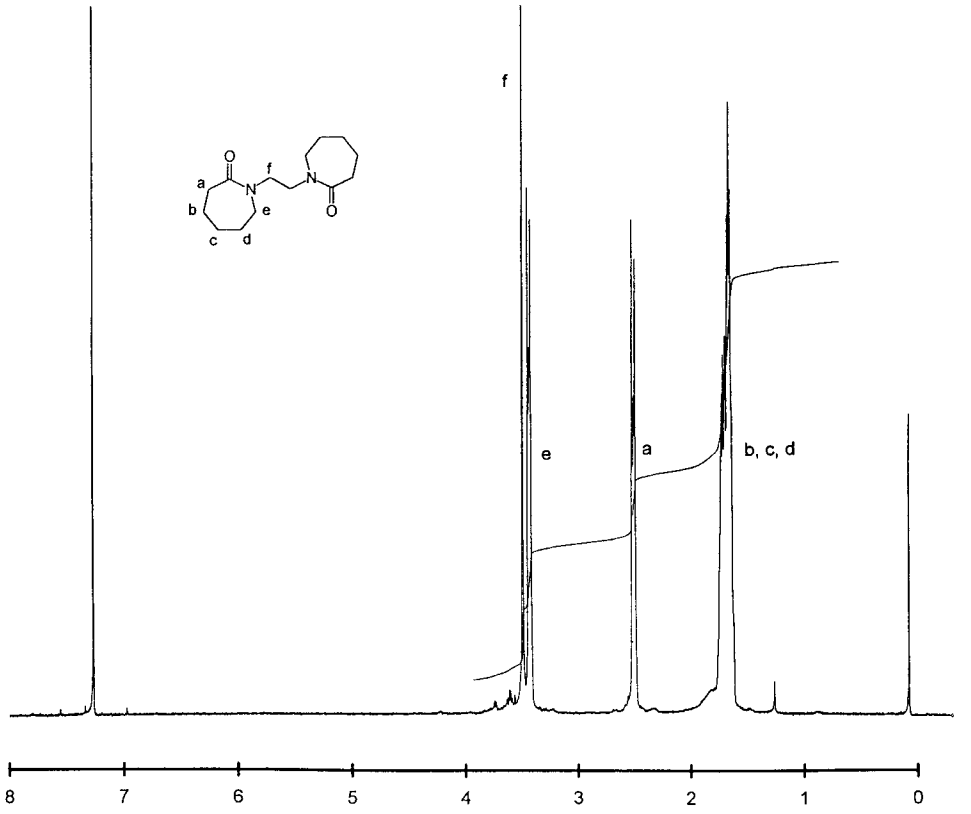
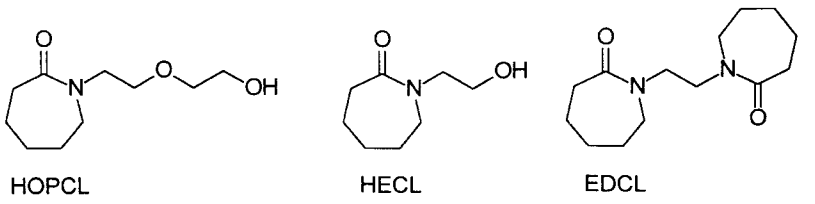


Figure 4. ^{1}H-NMR spectrum of c (EDCL), isolated from the reaction mixture with preparative HPLC.



Scheme 1. Ethylene glycol derivatives of caprolactam.

For the analysis of these linear species, a HPLC method was developed using post column derivatization with o-phtalaldehyde (OPA) in the presence of 3-mercaptopropionic acid. OPA is a selective agent [11] for primary amines forming UV-sensitive derivatives with maximal absorption at a wavelength of 340 nm. Separations were performed on a C18-column using an elution gradient prepared

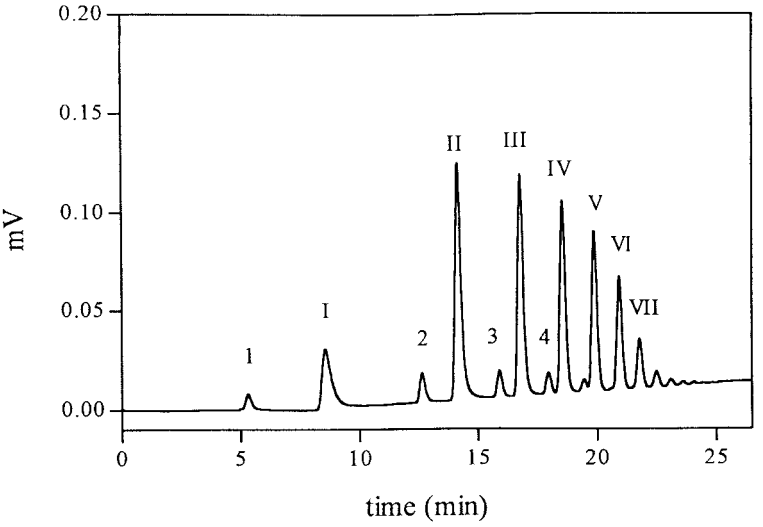


Figure 5. HPLC analysis (Post column derivatization with OPA) of the reaction mixture after 66 minutes, degradation at 250°C (1 = H-[NH(CH_2)$_5$CO]-OH, 2 = H-[NH(CH_2)$_5$CO]$_2$-OH,...; I = H-[NH(CH_2)$_5$CO]-O(CH_2)$_2$-OH, II = H-[NH(CH_2)$_5$CO]$_2$-O(CH_2)$_2$-OH,...).

from aqueous phosphate buffers (pH 3) containing 5% acetonitrile and 40% acetonitrile. The presence of caprolactam and N-substituted compounds does not interfere with the determination of these linear compounds since absorption is measured at a wavelength well above the absorption of those compounds.

A typical chromatogram of the reaction mixture is presented in Figure 5. For comparison, a mixture containing linear oligomers, obtained from an extraction process of the commercial production of nylon-6, was analyzed under the same conditions (Figure 6). These linear oligomers contain free carboxylic acid functions.

Comparing Figures 5 and 6 reveals that the linear oligomers with free carboxylic acid function are formed during glycolysis, however, it is evident that a more important homologues series of compounds is present in the reaction mixture. These compounds appeared to be the linear oligomers with esterified carboxylic acid function. This assignment is supported by the observation that the elution time of separately synthesized ethylene glycol ester of ε-aminocaproic acid corresponds with the elution time of the first compound of the series (I in Figure 5).

Definite proof for the structure was obtained by analysis of the reaction mixture by atmospheric-pressure chemical ionization (APCI) mass spectroscopy,

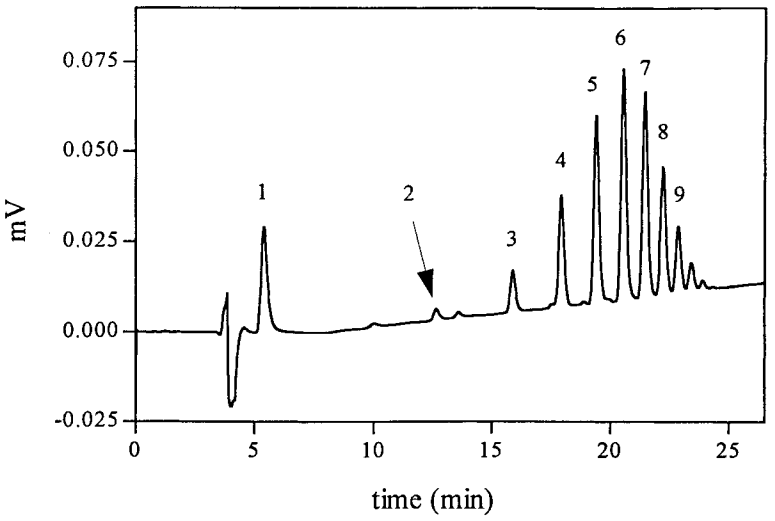


Figure 6. HPLC analysis of a mixture containing linear oligomers of caprolactam with free carboxylic acid groups (extract from commercial production mixture).

presented in Figure 7. APCI mass spectroscopy is a technique capable of analyzing high molecular weight compounds without major degradation. The apparatus was operated in the positive mode implying that the molecular ions have a mass that is one unit higher than the mass calculated from the molecular structure. The series of ions at m/z 176, 298, 402, 515, 328 and 741 correspond to the linear oligomers with esterified carboxylic acid functions (H-[$NH(CH_2)_5CO]_x$-$O(CH_2)_2$-OH, x = 1,2,3,4,5,6).

Partly Degraded Polymer

From a mechanistic viewpoint, it is interesting to know how the molecular weight and molecular weight distribution change during degradation. GPC is generally used for this purpose. However, the insolubility of nylon-6 in the classical GPC solvents complicates the analysis. Trifluoroacetic acid anhydride (TFAA) is a known derivatizing agent which converts the polyamide into a compound soluble in usual organic solvents such as tetrahydrofuran or chloroform [12, 13]. This method was described earlier by Schulz [12] and used without modification. The determination of the endgroup functionalities in the partly degraded polymers was performed with ^{1}H-NMR. ^{1}H-NMR spectroscopy of derived nylon-6 has been reported earlier for the investigation of copolymers of nylon-6 and polycarbonate

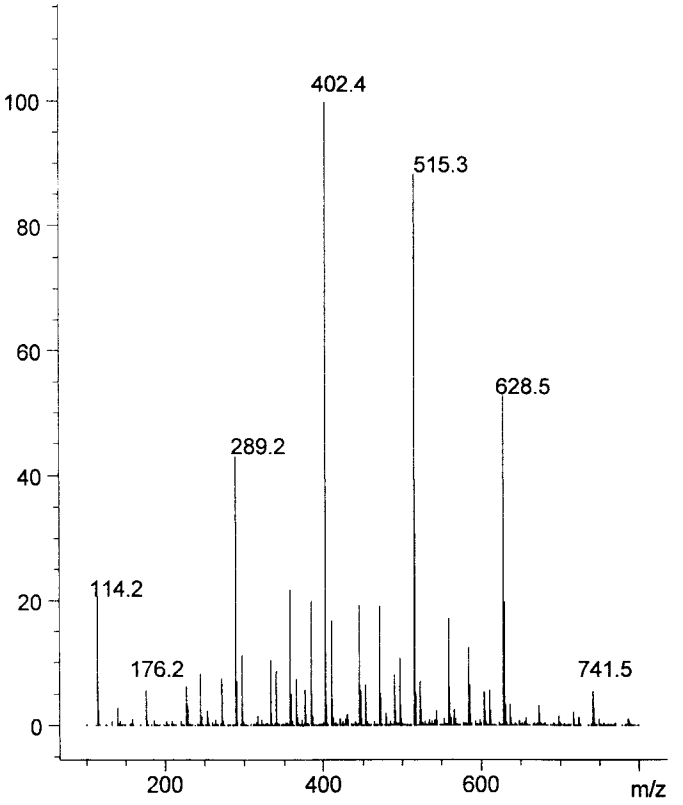


Figure 7. APCI mass spectrum of the total reaction mixture after 50 minutes, reaction at 250°C showing the presence of glycolate ester endgroups in the linear oligomers of caprolactam.

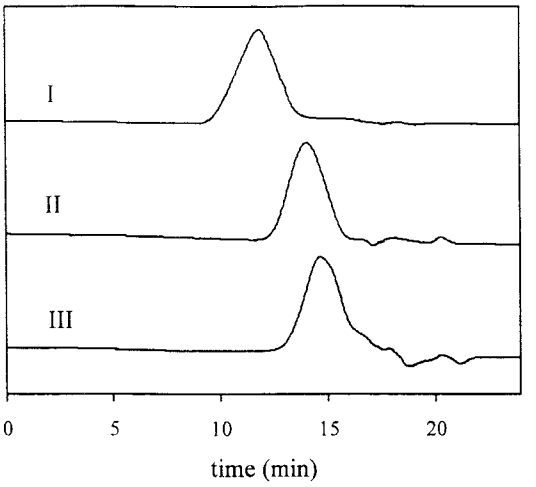
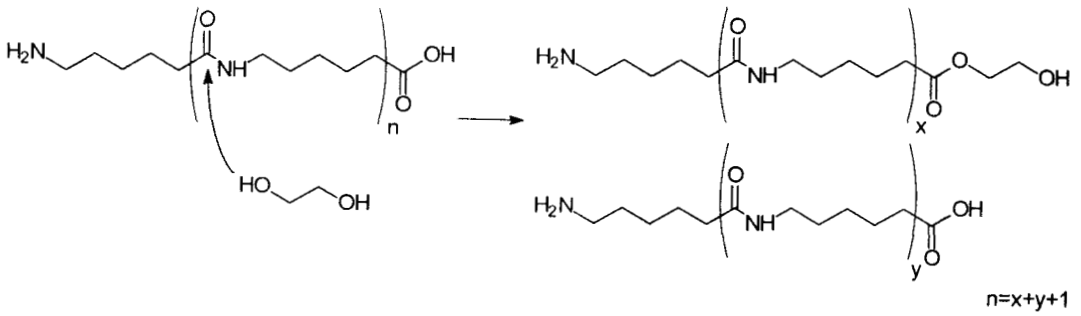
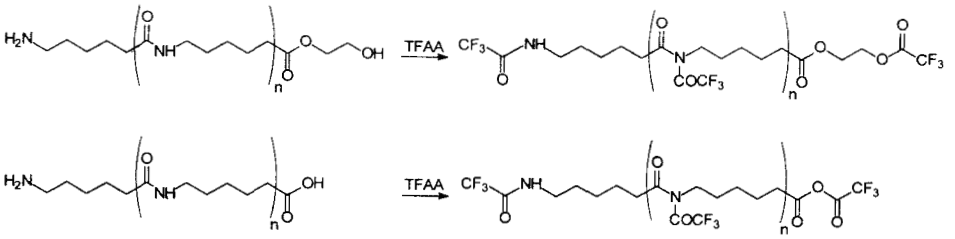


Figure 8. GPC analysis of the original polymer (I, M_n = 17100 g/mol, M_w = 57500 g/mol) and of two partly degraded samples (II, 5 minutes degradation, M_n = 1970 g/mol, M_w = 4030 g/mol; III, 110 minutes reaction, M_n = 4830 g/mol, M_w = 7430 g/mol).



Scheme 2. Glycolysis of polycaprolactam.



Scheme 3. Derivatization of polymer amide functions and endgroups with TFAA.

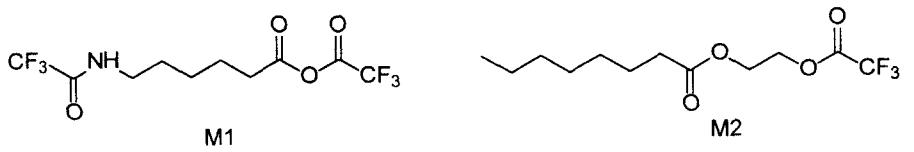
[14]. However, at our knowledge, no information has been reported on the nature of the endgroups.

Figure 8 presents GPC chromatograms of degraded polymer after different reaction times.

If chain scission in the polymer occurs by glycolysis of the amide function, ethylene glycol ester endgroups are formed (Scheme 2).

Besides the amide function in the polymer chain, also the amine endgroups, carboxylic acid endgroups and hydroxyl functions of the esterified carboxylic acid endgroups are expected to react with TFAA (Scheme 3).

To assign the signals in the ^{1}H-NMR spectrum of the partly degraded polymer, ε-aminocaproic acid and the glycol ester of caprylic acid were derivatized with TFAA and analyzed. The glycol ester of caprylic acid is a model for the esterified carboxylic acid endgroup (Scheme 4, M2), ε-aminocaproic acid is a model for both amine and the free carboxylic acid endgroup (Scheme 4, M1).



Scheme 4. Model compounds for TFA-derivatized polycaprolactam.

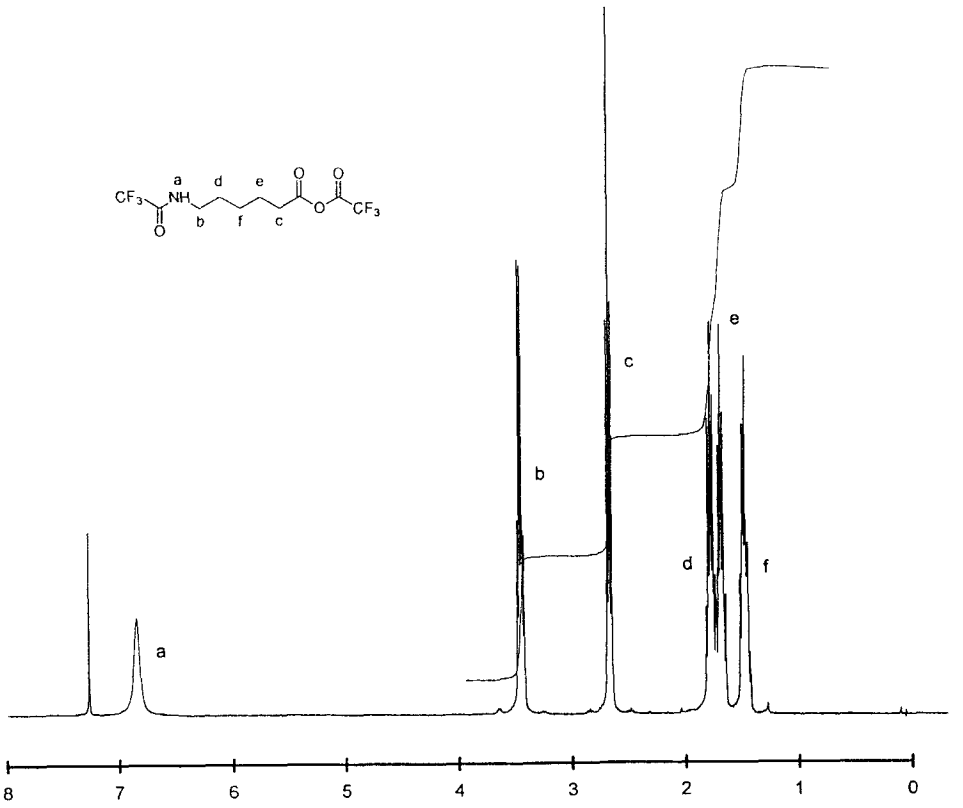


Figure 9. ^{1}H-NMR spectrum of TFA-derivatized ε-aminocaproic acid.

The spectra of the model compounds are shown in Figures 9 and 10. Figure 11 presents the ^{1}H-NMR spectrum of a partly degraded polymer. Comparison of this spectrum with the spectra of the model compounds shows that three kinds of endgroups are present: amine, carboxylic acid and ethylene glycol ester in a ratio 1/0.3/0.7.

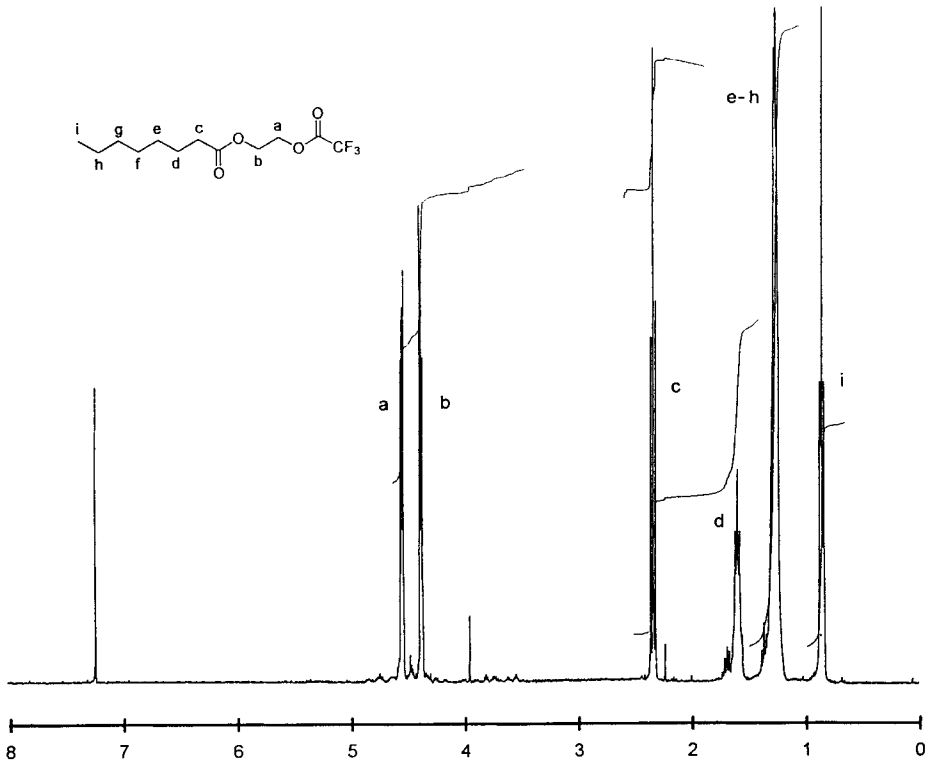


Figure 10. ^{1}H-NMR spectrum of TFA-derivatized caprylic acid.

Formation of a fraction of free carboxylic acid endgroup is explained by the hydrolysis of ester endgroups during the purification procedure.

CONCLUSION

Nylon-6 is degraded to linear oligomers and ultimately to a mixture of low molecular weight compounds by glycolysis in the presence of phosphoric acid at 250°C.

The formation of caprolactam, N-(2-hydroxyethyl)-caprolactam, N-(5-hydroxy-3-oxa-pentyl)-caprolactam, N,N'-ethylene-di(caprolactam) and linear oligo-mers with free carboxylic acid and with the carboxylic acid esterified with ethylene glycol was proven. No cyclic oligomers of caprolactam were found.

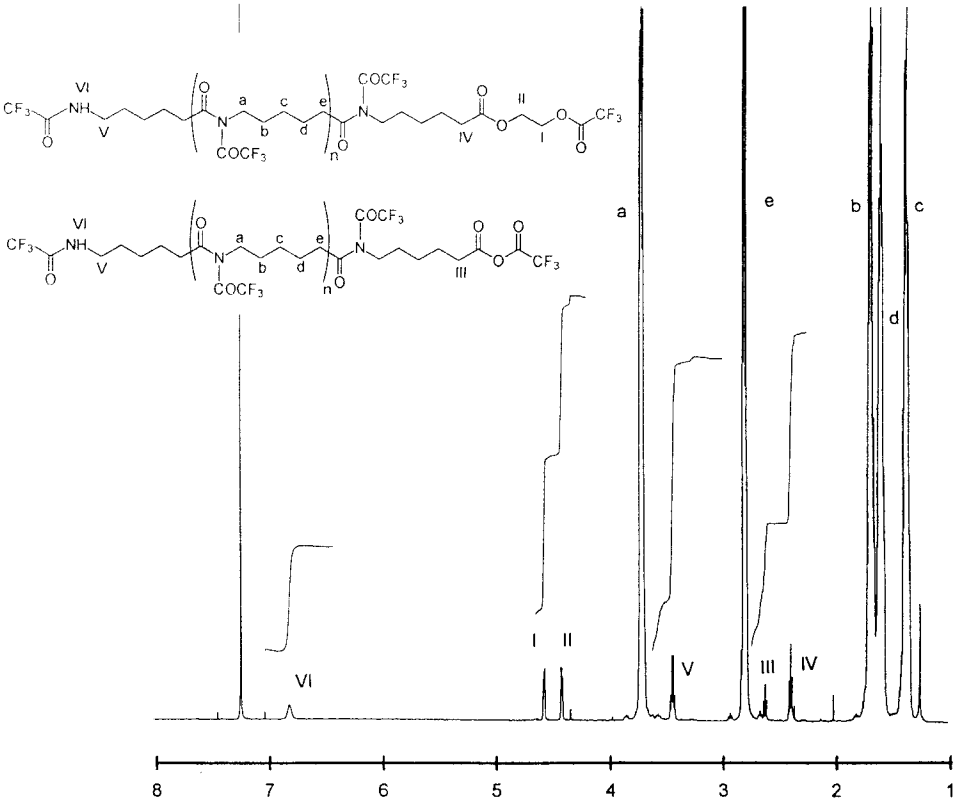


Figure 11. ^{1}H-NMR spectrum of TFA-derivatized polymer, isolated after 16 minutes degradation.

A ^{1}H-NMR spectroscopy study of partly degraded polymer showed that an amine function is present at the one end and carboxylic acid or ethylene glycol ester at the other end of the polymer.

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