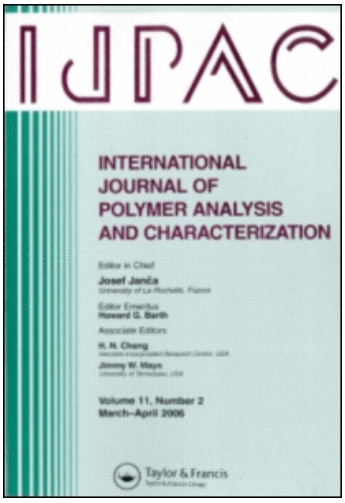

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Changes in Composition of Hydrolyzed Poly(butylene adipate-*co*-caproamide) Characterized by Pyrolysis-GC-MS, ^{1}H-NMR and FTIR

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The changes in composition of an abiotically degraded polyester-amide, poly(butylene adipate-*co*-caproamide), in an aqueous environment at 37°C; 60°C and 80°C were investigated. The changes in polymer composition were studied using pyrolysis-GC-MS, ^{1}H-NMR, FTIR, and size exclusion chromatography, and degradation products were analyzed by solid-phase extraction and subsequent GC-MS. During the degradation of PEA in an aqueous environment, the main degradation products were 6-aminohexanoic acid, 1-hydroxydodecanoic acid-6-one-5-oxo and dimers. After longer degradation times and at higher degradation temperatures, 1-hydroxydodecanoic acid-6-one-5-oxo was cleaved further into hexanedioic acid and 1,4-butanediol. At 80°C, the degradation was fastest with the largest weight loss due to dissolution of oligomer. At 80°C, the amide content in the copolymer increased with increasing degradation time. We suggest that there is a two-step degradation mechanism with the formation of linear degradation products, where the hydrolysis of ester bonds is favored over that of amide bonds.

Keywords: Polyester-amide; Hydrolysis; Degradation; Pyrolysis; Degradation products

INTRODUCTION

Biodegradable polymers have been studied extensively in biomedical, agricultural and packaging applications. Among these polymers,

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aliphatic polyesters are the most important due to their biodegradability and hydrolyzability. Aliphatic polyesters do not in general have good mechanical properties, but aliphatic polyamides, which do have good mechanical properties, lack biodegradability except for low-molecular weight polyamides[1] and α-amino acid-containing polyamides.[2–4] They are non-biodegradable because of their high degree of hydrogen bonding and regularity.[5] Aliphatic polyester-amides have therefore recently become more interesting as biodegradable polymers for medical and agricultural applications due to their better mechanical properties.

In a preliminary investigation of the microbial degradability of a polyester-amide, poly(butylene adipate-*co*-caproamide) (PEA), we observed that the polymer was sensitive to abiotic hydrolysis. Only a few researchers have studied the hydrolysis of polyester-amides. Barrows *et al.*[6] sought to combine the excellent fiber, film and molding properties of nylon with the degradability of polyglycolic acid by polymerizing a diamidediol with diacyl chloride and thus introducing hydrolytically unstable ester linkages into the polyamide structure. They showed that their polyester-amide could be degraded *in vivo* by hydrolysis and that it yielded non-toxic degradation products. Bueno Martínez *et al.*[5] studied the hydrolytic degradation of polyester-amides derived from carbohydrates and found that the degradation proceeds via breaking of ester linkage with the formation of cyclic monomeric end products. They concluded that the crystallinity and hydrophilicity of the polymer affects the rate of hydrolysis. Tokiwa *et al.*[7] studied the enzymatic hydrolysis of polyester-amides derived from polycaprolactone and different nylons. They showed that the susceptibility of the polyester-amides to hydrolysis by *Rhizopus delemar* lipase decreased with shortening of the polyamide blocks and with increasing polyamide content. Nagata[8] also studied the enzymatic hydrolysis of poly(hexamethylene adipate) copolymerized with aliphatic diamines and found that low crystallinity of the polyester-amides was the major factor increasing their degradation by *Rhizopus delemar* lipase.

Gonsalvez *et al.*[9] studied the degradation of non-alternating polyester-amides by two fungi, *Fusarium moniliforme* and *Aspergillus niger*. They found that *F. moliniforme* was able to degrade all the copolymers tested by ester hydrolysis, but that *A. niger* was less efficient. Grigat *et al.*[10] showed that the same type of polyester-amide as

in our study was degraded within 70 days in a composting test. Some hydrolytic studies of polyamide-6 (PA-6) and poly(butylene adipate) (PBA), i.e., the homopolymers of PEA, have also been carried out. It was shown that the hydrolysis of PA-6 is a relatively slow process and the polymer is simultaneously hydrolyzed both from the surface and in the bulk.[11,12] The hydrolysis of PA-6 is also catalyzed by the presence of salt and enzymes.[13] Doi and co-workers have studied the hydrolysis of PBA in natural waters.[13,14] The rate of degradation of PBA was dependent on the source of the natural water used. In lake fresh water, PBA lost 80% of its weight, whereas in river fresh water and in different seawaters, the weight loss varied between 11% and 34%.

The purpose of this study was to characterize the structural changes occurring in PEA and to relate these changes to degradability. A mechanism for the degradation of PEA in an abiotic aqueous environment at various temperatures is proposed.

EXPERIMENTAL

Materials

Films of poly(butylene adipate-*co*-caproamide) (BAK 1095) were used in this study. $M_w = 38\,100$ and $M_n = 14\,900$. The thickness of the film was 90 μm and the material was obtained from Bayer (Germany). Tenova AB (Sweden) processed the film. According to ^{1}H-NMR analysis, the amide content was 68% (73% with Fourier transform infrared spectrometry (FTIR)).

Standards used for pyrolysis-GC-MS were polycaproamide (PA-6) from Sigma-Aldrich and PBA oligomers. The PBA oligomers were prepared by melt polycondensation. A mixture (1 : 1) of 1,4-butanediol (Sigma-Aldrich) and hexanedioic acid (Sigma-Aldrich) was heated at 170°C for 2 h in a stream of nitrogen with a small amount of *p*-toluene sulphonic acid as an esterification catalyst. 6-Aminocaproic acid (Sigma-Aldrich) was also used as a standard.

Degradation Procedure

Degradation was performed in 22-mL glass vials containing a mineral medium and the polymer film samples, sealed with Teflon septa and aluminium caps. The flasks contained approximately 0.4 g of polymer film,

cut in pieces of 20 × 20 mm, and 16 mL of mineral medium. The mineral medium contained per liter of deionized water: 5.0 g $(NH_4)_2C_4H_4O_6$, 1.0 g KH_2PO_4, 1.0 g $MgSO_4 \cdot 7H_2O$, 0.8 mL $FeCl_3 \cdot 6H_2O$ (1% solution) and 8 mL $ZnSO_4 \cdot 7H_2O$ (1% solution). In addition, 0.5 mL of 0.02% (w/w) NaN_3 was added to each vial to maintain sterile conditions. The vials were kept in ovens for 70 days at 37°C, 60°C and 80°C and were sampled at regular intervals.

The effect of adding NaN_3 was investigated by subjecting the polymer to the same mineral medium without $(NH_4)_2C_4H_4O_6$ and NaN_3 for a period of 70 days at 60°C. There was no difference in weight loss or molecular weight between these samples and those kept at 60°C in the presence of NaN_3.

Sampling and Extraction of Degradation Products

The residual polymer was separated from the aqueous phase and was kept for further analysis.

Solid-phase extraction (SPE) was used to extract degradation products from the aqueous phase. Water-soluble degradation products were extracted with SPE columns (100 mg C8 from Sorbent AB). One mL of aqueous sample was adjusted to pH 1–2. The SPE column was solvated with 1 mL of methanol (HPLC-grade, Kebo Lab AB), and preequilibrated with 1 mL of mineral medium (the same as in the sample) pH-adjusted to 1–2. The sample solution was then applied to the column and, after subsequent drying of the column, the degradation products were eluted with 1 mL of methanol. The eluate was then analyzed with GC-MS.

Methods

Thermal Analysis

Thermal analysis was performed in a Mettler-Toledo TGA/SDTA 851^e system in an inert atmosphere (nitrogen). The temperature was raised from 30°C to 900°C at a rate of 10°C/min.

Pyrolysis-Gas Chromatography-Mass Spectrometry (Py-GC-MS)

The pyrolysis was performed in a Pyrola® filament pulse pyrolyser (PyroLab AB, Sweden) equipped with a Pt filament. About 10 μg of

polymer film was pyrolyzed for 2 s at 600°C. The volatile products were then separated directly in a Perkin-Elmer gas chromatograph model 8500 with a split/splitless injector. The GC was coupled to a Perkin Elmer ITD mass spectrometer (EI or CI (methane) mode). The GC was equipped with a DB-5MS capillary column from J&W (30 m × 0.32 mm i.d.). Helium was used as carrier gas (1 mL/min). The temperature program of the column started at 40°C and increased to 300°C (10°C/min). The injector temperature was held at 275°C.

Fractionated pyrolysis was performed with about 100 μg of polymer film, which was pyrolyzed for 2 s at 400°C, 500°C and 600°C in a sequence to separate different thermo-labile fractions of the polymer.

Nuclear Magnetic Resonance (^{1}H-NMR)

^{1}H-NMR spectra of 10 μg polymer in 0.5 mL dimethylsulfoxide-*d6* were recorded at 400 MHz on a Bruker AC-400 using Bruker software. The copolymer composition, expressed as the mole percentage of amide, is the ratio of peak areas due to the CO–O–$\mathbf{CH_2}$ methylene groups in the ester at 4.01 ppm and due to the NH–$\mathbf{CH_2}$ methylene group at 2.99 ppm.

Fourier Transform Infrared Spectrometry (FTIR)

The FTIR analysis was performed on a Perkin-Elmer 2000X spectrometer equipped with a Golden Gate refractive unit with a diamond crystal. Spectrum 2000 was used to evaluate the spectra. Scan range: 4000–600 cm^{-1}. Resolution: 4 cm^{-1}. Number of scans: 20.

Size Exclusion Chromatography (SEC)

The change in molecular weight during the degradation was analyzed by SEC. The instrument was equipped with a Waters 6000A pump, a PL-EMD 960 light scattering evaporative detector, two PL gel 10 μm mixed-B columns (300 × 7.5 mm) from Polymer Labs (UK) and one Ultrahydrogel linear column (300 × 7.8 mm) from Waters Corp. (USA). Dimethylformamide was used as mobile phase at 70°C and at a flow rate of 1 mL/min. The system was calibrated with poly(ethylene oxide) standards. Each sample was analyzed four times to obtain an appropriate average of the molecular weight.

Gas Chromatography-Mass Spectrometry (GC-MS)

The degradation products were identified and quantified in a Finnigan GCQ gas chromatograph/mass spectrometer (EI or CI (methane) mode). The GC was equipped with a Rtx®-5MS capillary column (Crossbond® 5% diphenyl–95% dimethyl polysiloxane) (30 m × 0.25 mm i.d.) from Restek Corp. (USA). Helium was used as carrier gas. The temperature program of the column was: 40°C for 10 min, followed by a rise in temperature from 40°C to 250°C at 10°C/min. The injector temperature was held at 200°C.

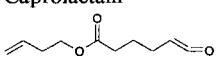
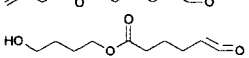
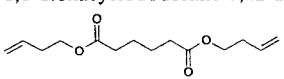
RESULTS AND DISCUSSION

Pyrolysis of PEA

When polylactams are pyrolyzed, they undergo an intra-molecular amide exchange process producing cyclic oligomers.[15] The primary thermal decomposition reaction of the aliphatic polyesters produced from dialcohols and dicarboxylic acids is also an intra-molecular exchange. From the thermal degradation reaction, cyclic oligomers are formed. These cyclic esters may undergo secondary fragmentation (β-CH hydrogen transfer) during MS analysis and they are therefore difficult to detect.[16] Plage *et al.*[17] showed that when diol-dicarboxylic acid polyesters containing butylene and adipate sequences are pyrolyzed, other products may also be formed. A pyrolytic product originating from butylene subunits is butadiene. Adipic subunits produce butyrodiketene, cyclopentanone and cyclic anhydrides. Another study showed that, during the pyrolysis of poly(butylene adipate) above 300°C, cyclic oligomers and dehydration products are the most prominent pyrolytic products.[18]

In order to find the optimal pyrolysis temperature, thermal analysis and fractionated pyrolysis were run on original PEA film. Thermal analysis showed that the sample was degraded in a single step at about 500°C. Fractionated pyrolysis was performed for 2 s at 400°C, 500°C and 600°C in sequence on approximately 100 μg of sample, and it was found that the largest amount and range of products were produced at 600°C. Table I shows the products formed during the pyrolysis of PEA at 400°C, and 500°C and 600°C. A homologuous series of doublet peaks was also produced, but they have not yet been identified.

TABLE I Products formed during the pyrolysis of unaged PEA at 400°C, 500°C and 600°C

Peak number in Figure 2	*Retention time* (min)	*Compound*	*Ion*[c] *CI* (*m/z*)	*Ions*[d] *EI* (*m/z*)	400°C[e]	500°C[e]	600°C[e]
1	02:05	1,3-Butadiene	55	26, **39**, 54		+	+
2	04:46	Cyclopentanone	85	27, 39, 55, **85**		+	+
3	06:03	Unknown *m/z* 127[a]	127	27, **39**, 55, 127			+
4	06:13	Unknown *m/z* 129[b]	129	**27**, 39, 57, 129			+
5	06:26	Pentanoic acid	103	**27**, 39, 60, 85, 103			+
6	07:09	1,4-Butanediol	91	**31**, 55, 73, 91			
7	07:39	Unknown *m/z* 141[a]	141	27, **39**, 55, 69, 141			+
8	07:50	Unknown *m/z* 143[b]	143	27, **39**, 55, 71, 143			+
9	08:03	Hexanoic acid	117	27, **39**, 60, 99, 117			+
10	09:22	Unknown *m/z* 155[a]	155	27, 39, **55**, 83, 101, 155			+
11	09:36	Unknown *m/z* 157[b]	157	**27**, 39, 55, 85, 114, 157			+
12	11:07	Unknown *m/z* 169[a]	169	27, **39**, 55, 69, 97, 115, 169			+
13	11:18	Unknown *m/z* 171[b]	171	27, **39**, 55, 71, 99, 171			+
14	12:53	Caprolactam	114	39, 56, 85, 96, **114**	+	+	+
15	15:39		182	**39**, 55, 110, 182		+	+
16	16:42		201	**39**, 55, 111, 129, 183, 201	+	+	+
17	17:15	1,6-dioxacyclododecane-7,12-dione	201	**41**, 55, 115, 201		+	+
18	19:21		255	39, **55**, 111, 129, 183, 255		+	+

[a,b]Homologous series of peaks not yet identified. [c]Molecular ion in chemical ionization mode. [d]Main ions (bold types denotes base peak) in electron ionization mode. [e]Pyrolysis products of unaged PEA.

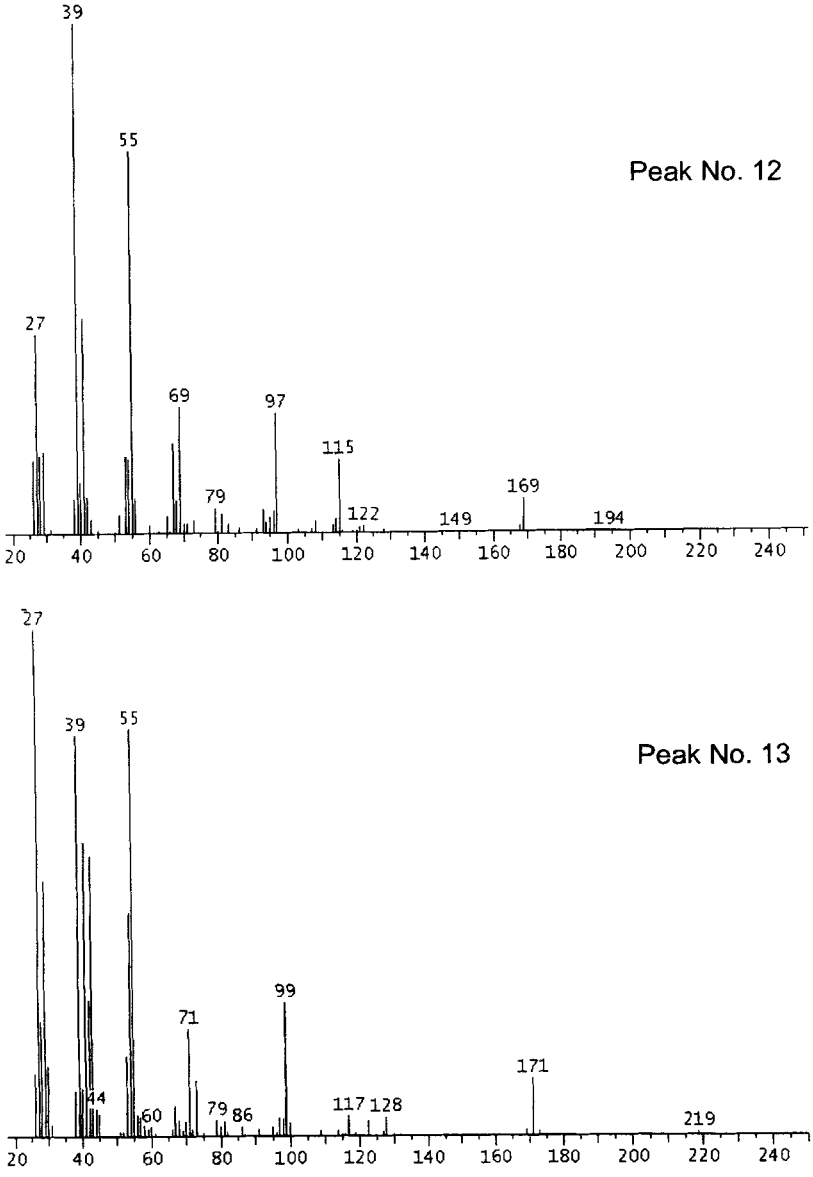


FIGURE 1 The mass spectra of one doublet (peak No. 12 and 13 in Table I) in the unknown homologous series produced during pyrolysis of PEA at 600°C.

Figure 1 shows the mass spectra of one doublet. When poly(butylene adipate) was pyrolyzed at 600°C, the doublet peaks also appeared. We therefore conclude that they originate from the ester part of PEA. Most of the other products have been identified from their mass spectra. The pyrolytic products have also been analyzed by chemical ionisation to confirm the interpretation.

Changes in Polymer Composition and Molecular Weight

Pyrolysis has been used to determine the monomer composition in copolymers,[19] but there are problems associated with such a determination. In order to determine the monomer composition quantitatively with Py-GC, a calibration with copolymers of the same type and with known compositions is necessary. We have also found that the two polymer parts in PEA do not degrade by the same mechanism at a given temperature. The polyester part of PEA yields several products during pyrolysis, while the polyamide yields only caprolactam. We have therefore used Py-GC only for a qualitative analysis of the monomer composition of the copolymer.

It was found that fractionated pyrolysis provided most information regarding structural changes in PEA at different stages of degradation. Figure 2(a)–(c) shows the pyrograms of PEA degraded for 10 weeks at 37°C, 60°C and 80°C, and pyrolyzed at 400°C, 500°C and 600°C. Figure 2(b) and (c) shows that the amide content in the copolymer increased during degradation at 80°C. Degradation at 37°C and 60°C did not change the monomer composition, but degradation at 80°C led to a large increase in the area of the caprolactam peak. The peaks relating to the ester part decreased significantly. Figure 2(a) indicates that, on subsequent pyrolysis at 400°C, PEA degraded at 37°C and 60°C produced no butanediol, whereas PEA degraded at 80°C did produce butanediol. This behavior is probably due to the residual degradation products inside the polymer matrix.

To confirm the Py-GC results, FTIR and ^{1}H-NMR analyses were carried out. The major FTIR absorption features of the amide group appeared at 1637 cm^{-1} (C=O stretching) and 1538 cm^{-1} (NH bending) and those of the ester group at 1729 cm^{-1} (C=O stretching) and 1165 cm^{-1} (C–O anti-symmetry stretching). The composition of copolyester-amides can be determined from the ratio of the

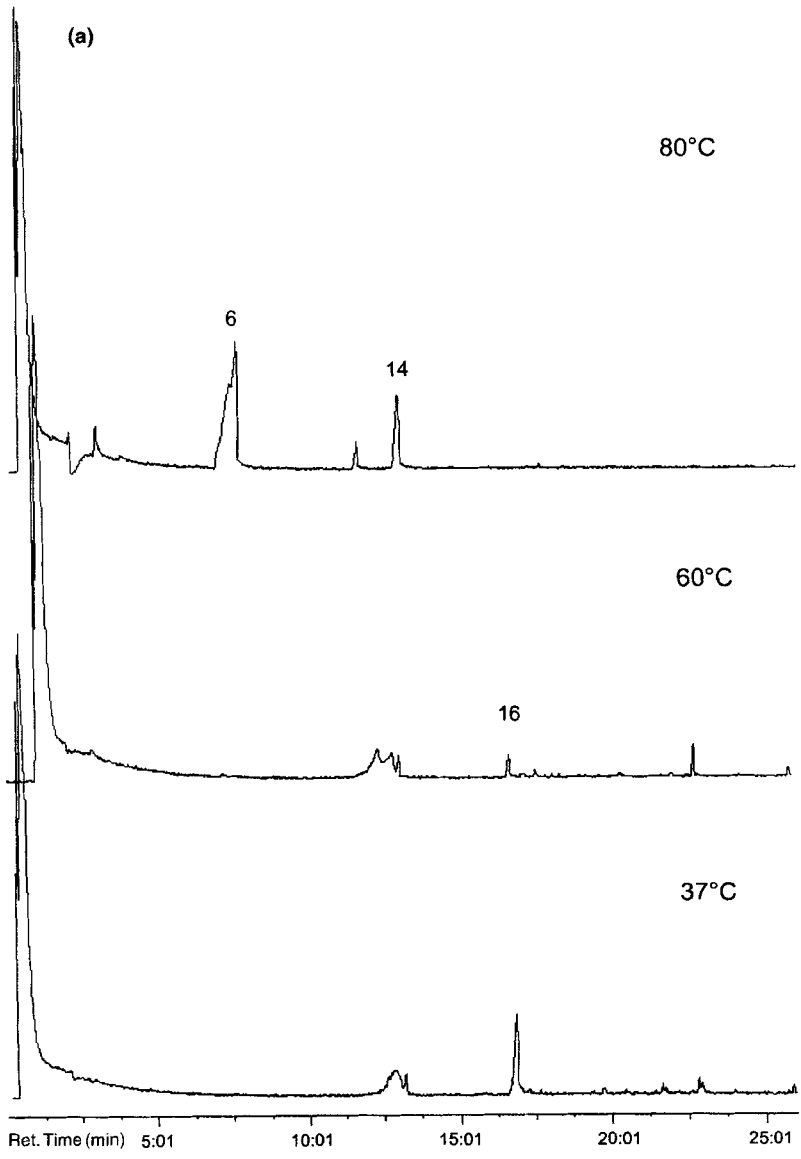


FIGURE 2(a)

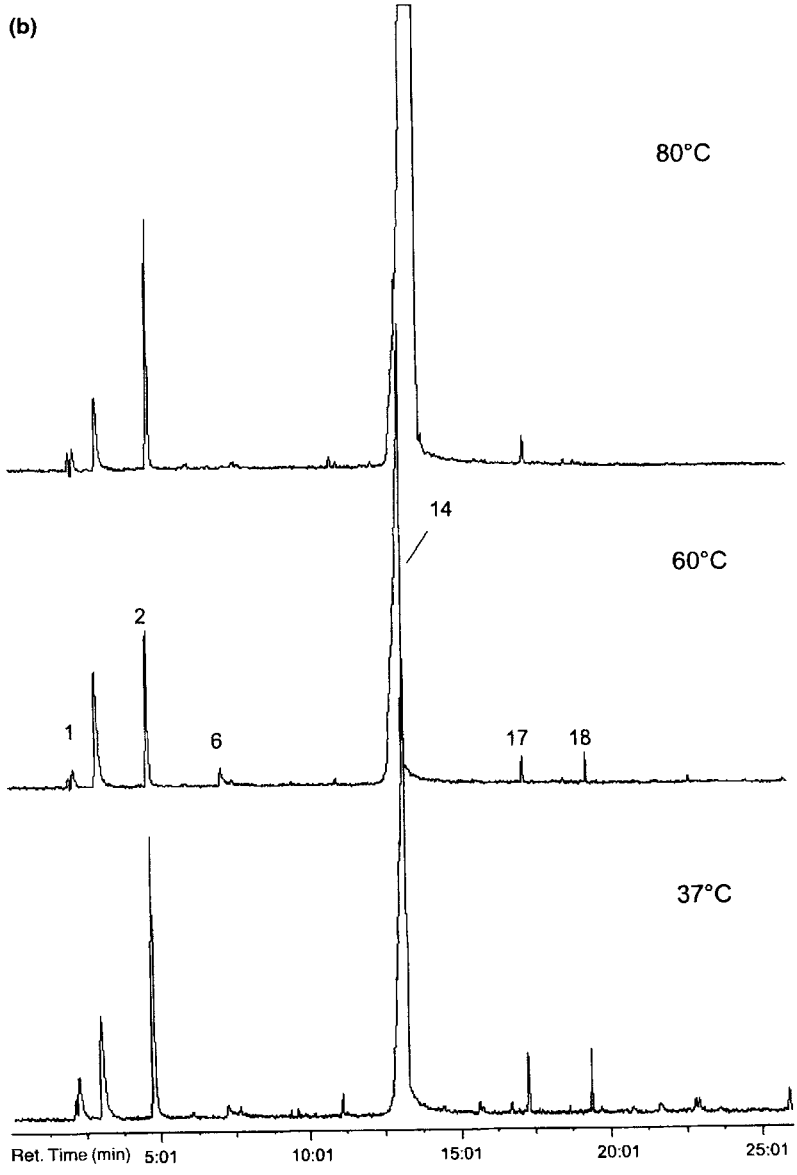


FIGURE 2(b)

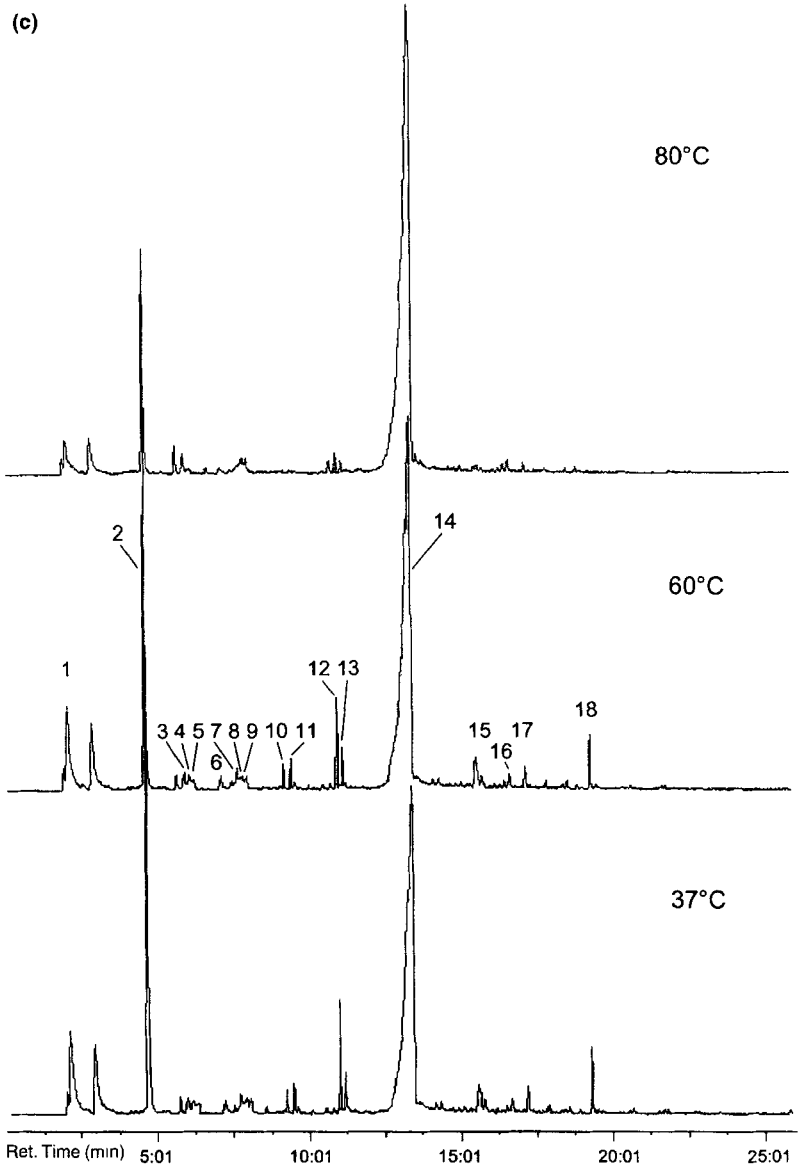


FIGURE 2(c)

FIGURE 2 The pyrograms of PEA degraded in sterile medium at 37°C 60°C and 80°C for 10 weeks. Fractionated pyrolysis at 400°C (a), 500°C (b) and 600°C (c) in He. Peak assignments are shown in Table I.

IR absorbances at 1637 cm^{-1} (A_A) and 1729 cm^{-1} (A_E).[20] The values of $2A_A/(2A_A + A_E)$ are shown in Figure 3(a). The original amide content of PEA was 73% (as measured with FTIR) and during degradation at 3°C and 60°C there was no significant change in composition. At 80°C, however, an increase in amide content was evident. Figure 3(b) shows the changes in amide content as measured with ^{1}H-NMR, and the same trend is observed.

Figure 4(a) shows the number-average molecular weight of PEA degraded at 37°C, 60°C and 80°C. The molecular weight decrease of PEA was, as expected, greatest during degradation at 80°C and smallest during degradation at 37°C. Figure 4(b) shows that the polydispersity decreased during degradation from a value of 2.6 to values below 2, which indicates nonrandom chain scission with preferential cleavage near the center of the molecule.[21,22]

These results shows that hydrolysis takes place preferentially at the ester bonds of the polyester-amide. Other authors have also observed this phenomenon when other types of polyester-amides have been hydrolyzed.[7,23,24] Hu *et al.*[25] compared the degradation of PA-6 with a blend of PA-6 and polylactide (90% PA-6) during hydrolysis at 80°C. The blend was hydrolyzed faster than the pure PA-6 and these results show that the hydrolysis of PA-6 is slower than that of the polyester. Polylactide is known to be easily hydrolyzed at higher temperatures, while PBA is more resistant. Even so, the results indicate that the hydrolysis of PA-6 is slower than of PBA.

Degradation Products

When PEA is degraded in a sterile mineral medium, the main degradation products are caprolactam, 1,6-dioxacyclododecane-7,12-dione and dimers according to GC-MS. Figure 5(a) and (b) shows the formation of degradation products with time and temperature. At longer degradation times and at higher degradation temperatures, 1,6-dioxacyclododecane-7,12-dione was further cleaved into hexanedioic acid and 1,4-butanediol. 1,6-dioxacyclododecane-7,12-dione was identified from the NIST MS-library. The dimers were identified from their mass spectra. The methylated products in Figure 5(a) and (b) originate from a reaction with methanol during extraction.

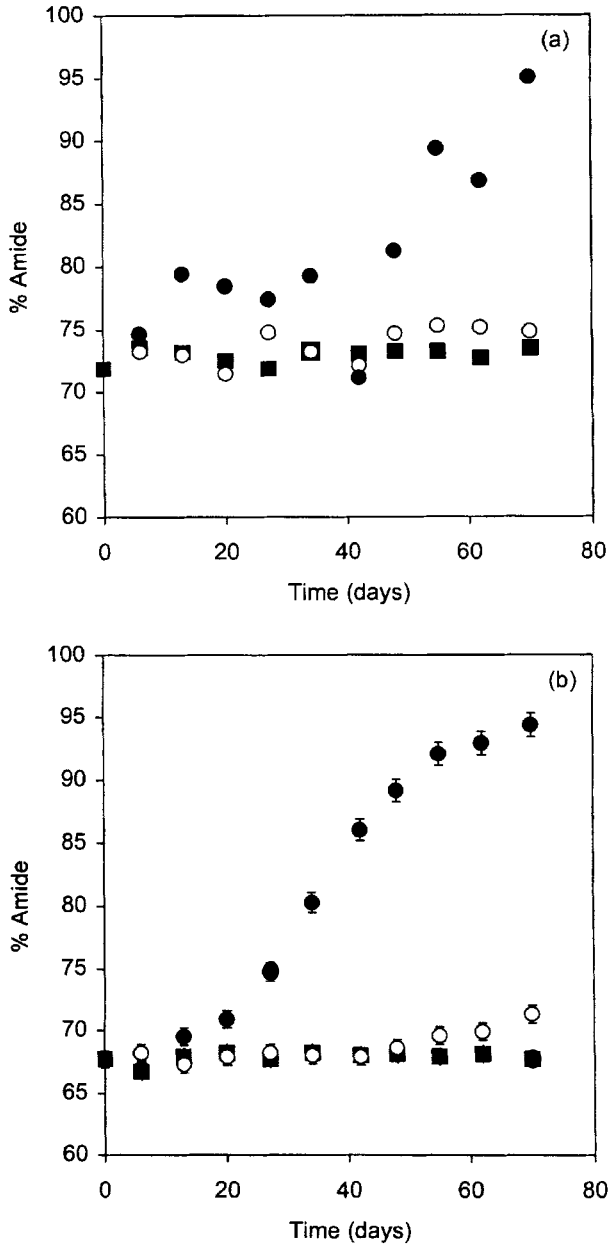


FIGURE 3 The amide content of PEA during degradation 37°C (■), 60°C (○) and 80°C (●) according to (a) FTIR and (b) ^{1}H-NMR.

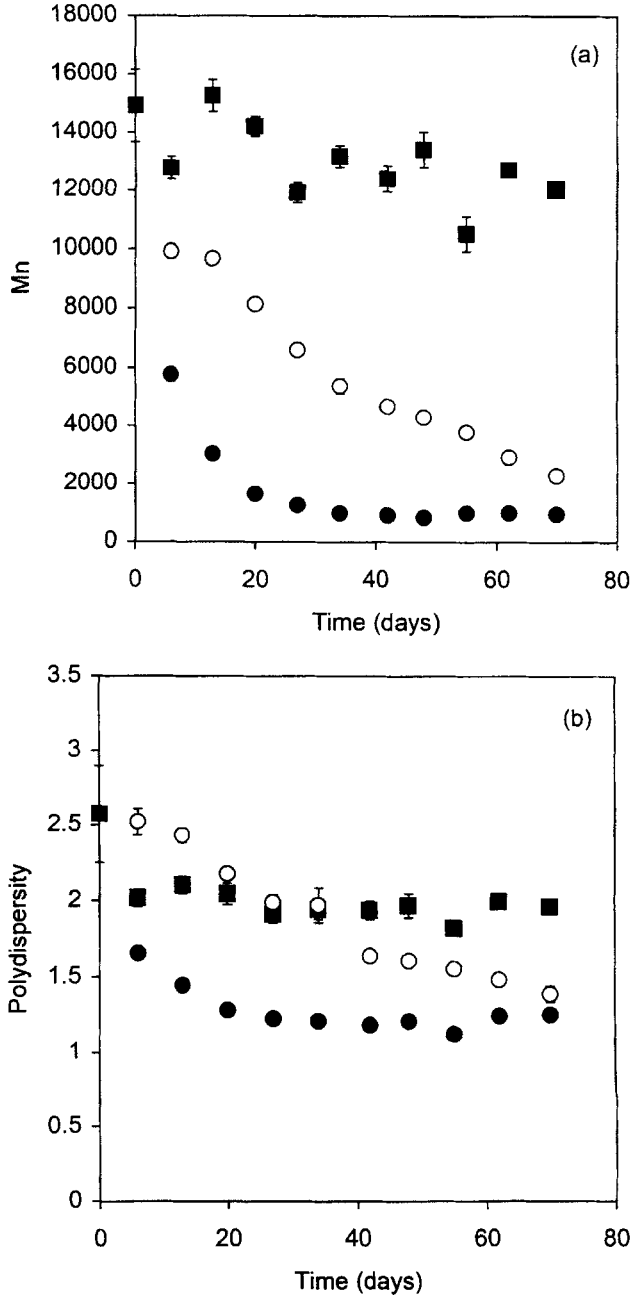


FIGURE 4 (a) Number-average molecular weight (M_n) and (b) polydispersity of PEA degraded in a sterile mineral medium at 37°C (■), 60°C (○) and 80°C (●).

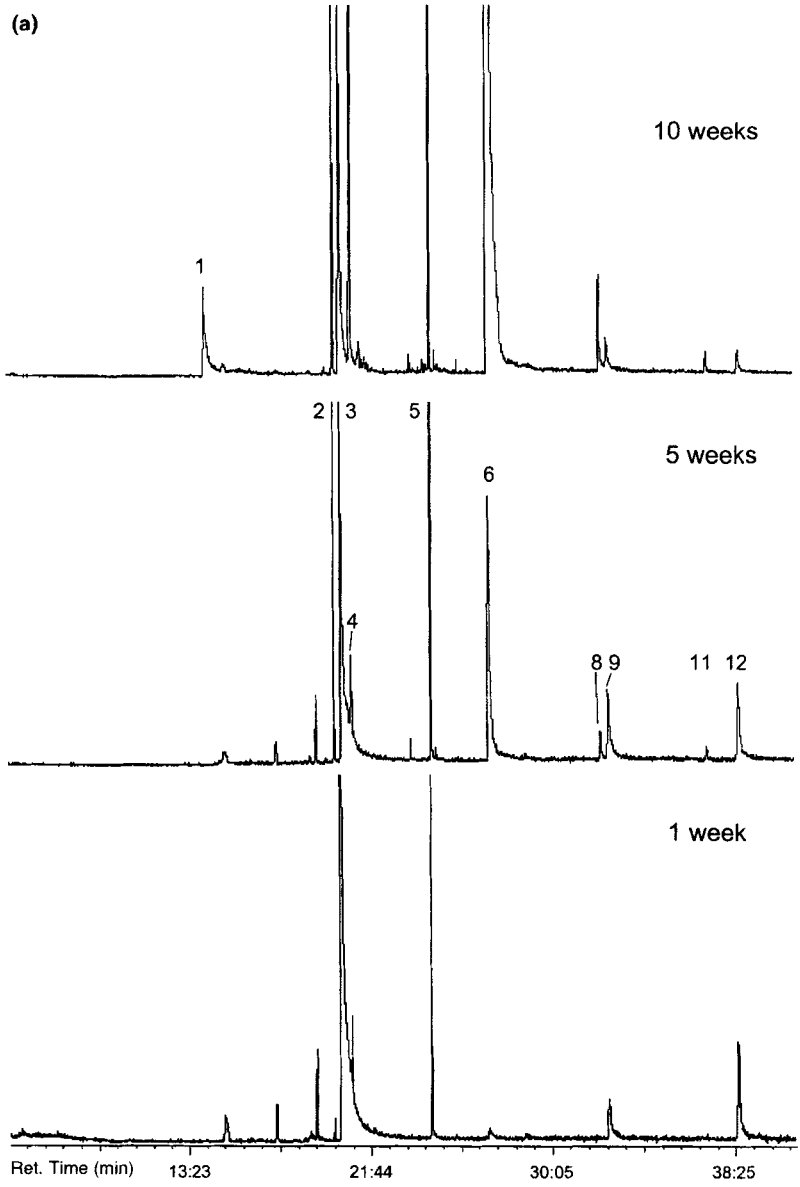


FIGURE 5(a)

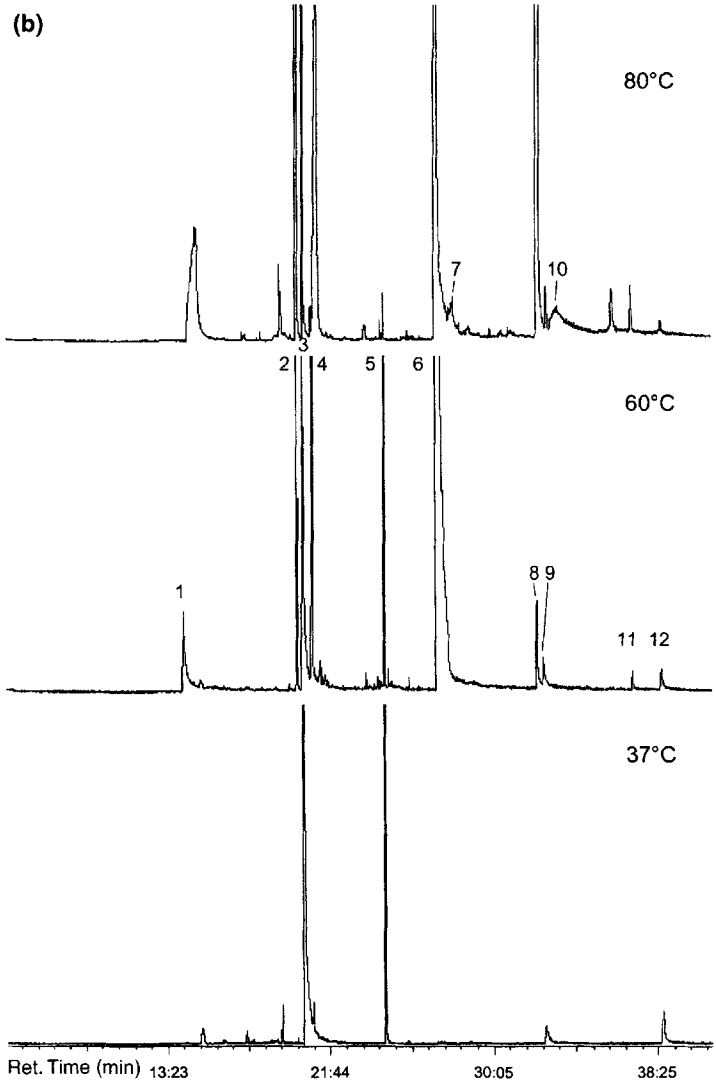


FIGURE 5(b)

FIGURE 5 Degradation product generation with (a) time (1, 5 and 10 weeks) at 60°C, (a) and (b) temperature (37°C, 60°C and 80°C for 10 weeks) (b). Peaks: 1,4-butanediol (1); hexanedioic acid, dimethyl ester (2); caprolactam (3); hexanedioic acid, monomethyl ester (4); 1,6-dioxacyclododecane-7,12-dione (5); 1-hydroxyundecanoic acid-6-one-5-oxo, methyl ester (6); 1 -hydroxy undecanoic acid-6-one-5-oxo (7); methyl ester of ester-amide dimer (sequential order unknown) (8); 1,7-diazacydotetradecane-6,13-dione (9); mixture of ester-amide dimer and 1,16-dihydroxydibutylhexanoate (10); 1-hydroxytricosanoic acid-6,11,18-trione-5,12,17-trioxo, methyl ester (11); 1-aza-cyclooctadecane-13,18-dioxo-7,12,19-trione (12).

It has been reported that caprolactam was formed during glycolysis of PA-6 at 270°C but that the oligomers were linear.[26] It has also been reported that there is an equilibrium between 6-aminocaproic acid and caprolactam in an aqueous environment.[27] In order to investigate whether the observed cyclic monomers and oligomers are formed during hydrolysis, during extraction or during GC analysis, the corresponding linear monomer, 6-aminocaproic acid, was extracted from the mineral medium and/or dissolved directly in methanol and then analyzed with GC-MS. The corresponding linear monomer of 1,6-dioxacyclododecane-7,12-dione was not available as a standard. It was found that the linear 6-aminocaproic acid was partly transformed into caprolactam during GC analysis. We also investigated the degradation products with reflection FTIR and this method indicated that the sample solution did not contain caprolactam. We therefore conclude that the cyclic monomers and oligomers are not formed during hydrolysis. They are simply ring-closed during analysis.

After five weeks of degradation at 80°C, a white powder precipitated from the aqueous solution when it was cooled to room temperature. FTIR and ^{1}H-NMR analyses of the powder indicate that it is an oligomer including both monomers (Figure 6(a) and (b)). Py-GC-MS analysis showed that the oligomer was largely amide. According to ^{1}H-NMR analysis, the amide content was 92%. This degradation product was not observed during degradation at 37°C or 60°C. Figure 7 shows that the weight loss of PEA was much greater during degradation at 80°C than at lower temperatures. We believe that the powder-degradation product is not soluble in the aqueous mineral medium at 60°C and thus does not leave the polymer matrix, even though it may have been formed during degradation. At 80°C, the product is dissolved in the medium and this leads to the large weight loss of the material. Yoon *et al.*[28] showed that this type of weight loss of polyesters undergoing hydrolysis corresponds to a dissolution of large oligomers by the surrounding medium.

CONCLUSIONS

The results presented in this work demonstrate the nonrandomness of the degradation of PEA. PEA was degraded in an abiotic aqueous environment at 37°C, 60°C and 80°C and the degradation was fastest

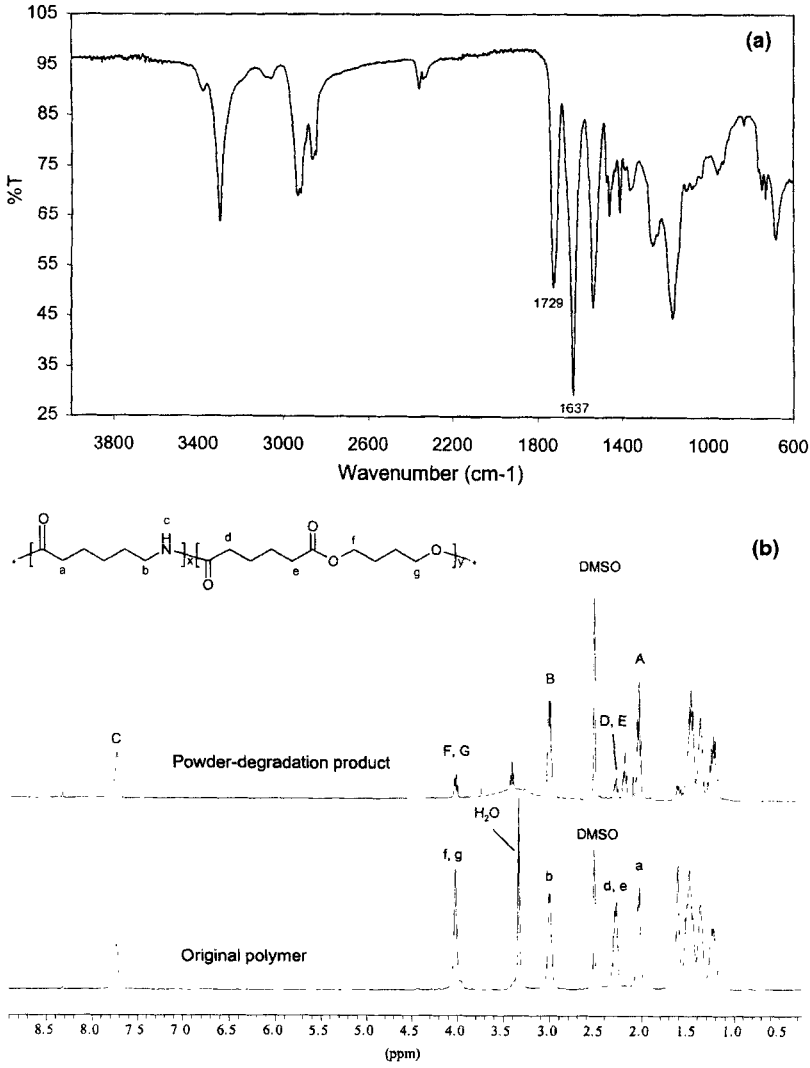


FIGURE 6 (a) The FTIR-spectra and (b) ^{1}H-NMR spectra of the powder produced during degradation in a sterile mineral medium at 80°C.

at 80°C. The amide concentration in the copolymer increases as a result of the degradation and we suggest that this is due to differences in hydrolyzability of the two homopolymers, i.e., polyamide-6 and poly(butylene adipate).

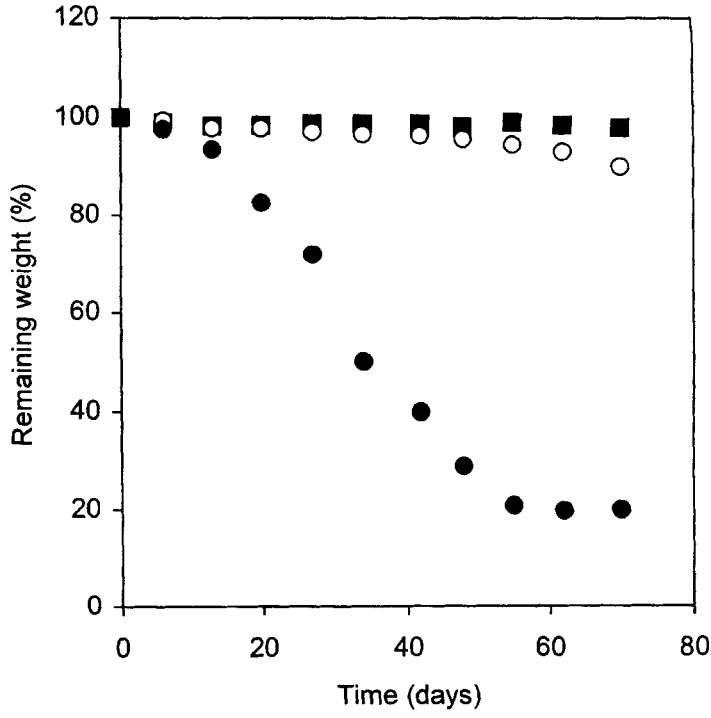


FIGURE 7 Weight loss of PEA degraded in sterile mineral medium at 37°C (■), 60°C (○) and 80°C (●).

Molecular weight determinations showed that the hydrolysis proceeded by nonrandom chain scission with preferential cleavage near the center of the molecules. Analysis of the degradation products indicates that the hydrolysis of PEA proceeds by a two-stage process. The copolymer is first hydrolyzed to 6-aminocaproic acid and 1-hydroxyundecanoic acid-6-one-5-oxo. 1-hydroxyundecanoic acid-6-one-5-oxo is then further hydrolyzed to 1,4-butanediol and hexanedioic acid.

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