Identification of Caprolactam Oligomers and Related Compounds in Aqueous Extracts of Nylon-6

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ABSTRACT: Cyclic oligomers of caprolactam were isolated from a multilayered polyolefin plastic film containing a nylon-6 layer and subsequently characterized. Nylon-6 was extracted with aqueous solutions and the levels of the oligomers were measured in the resulting extracts. Oligomers up to $n = 5$ were present at high and comparable levels in all the nylon-6 extracts. The levels of the oligomers dropped off rapidly with increased compound size after $n = 5$, with the heptamer being barely observable in the extract chromatograms. The effect of extracting solution pH on the compound's concentration in the extract was small, except for the monomer, whose accumulation was significantly decreased at low pH. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 95: 1262–1274, 2005

Key words: extractables; polyamides; degradation; nylon; oligomers

INTRODUCTION

Plastic materials are commonly used in the packaging of pharmaceutical and food products. The compatability of the package/product couple is impacted by the degree to which these two phases (plastic package and product) interact. Such an interaction may involve sorptive processes, by which one or more product components are taken up by the package, or extractive processes, by which one or more package compounds are leached into the product.

ε-Caprolactam is an extractable substance that has been associated with polyolefin-type packaging materials.[1,2] ε-Caprolactam is the monomer of polyamide 6 (nylon) and is a potential degradation product of materials commonly used in polyurethane adhesives.[1] Its presence in solutions stored in poly(vinyl chloride) containers manufactured within a polyolefin overwrap[1] and in polyolefin containers, especially after gamma irradiation,[2,3] has been reported. Because the production of high molecular weight polymers (such as polyamides) is often accompanied by the formation of moderate molecular weight oligomers,[4,5] it not unexpected that such polymers would contain cyclic and open chained oligomers,[6] with oligomers up to the hexamer being reported and quantitated.[6,7] Such oligomers, along with the unreacted monomer, represent the extractable portions of polycondensate polymers.[8] In fact, cyclic oligomers of caprolactam are reportedly present in water extracts of polyamides (e.g., waste solutions associated with nylon-6 production).[9]

The reported presence of caprolactam in packaged solution products, along with the reported existence of higher molecular weight oligomers in packaging materials, suggests that such oligomers may also be present in aqueous solutions contacted by either nylon-6 itself or nylon-6–containing materials. To investigate this possibility, cyclic oligomers of caprolactam were isolated from a multilayered polyolefin plastic film containing a nylon-6 layer and characterized. Nylon-6 was then extracted with aqueous solutions and the levels of the oligomers were measured in the resulting extracts.

EXPERIMENTAL

Materials

Nylon-6 resin, obtained from Aldrich Chemical (Milwaukee, WI), was used in all the quantitative extractions. Additional extractions, executed for the purpose of isolation and characterization, were performed on a multilayer laminated polyolefin film that contained nylon-6 as one of the intermediate layers. All analytical reagents used in this study were obtained as analytical grade from commercial vendors.

Compound isolation and identification

Extraction

Initial test samples, obtained primarily for screening purposes, were obtained by sequential extraction of

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the polyolefin film material with 40/60 ethanol/water. Specifically, approximately 35 g of material was subjected to three sequential extractions (same material extracted with three fresh portions of solution), with each extraction occurring at 70°C for 1 day or more. The material was cut into pieces to facilitate contact between the material's inner nylon layer and the extracting solution. To produce a more concentrated sample for analysis, each extract was concentrated by rotary evaporation and the individual concentrated extracts were combined and further concentrated by the same means.

A second, more concentrated, test sample, used for target isolation and characterization, was generated by the extraction of the approximately 130 g of nylon-6 material with a 40/60 ethanol/water solution (70°C for 3 days). The equivalent of about 80% of this extract was injected onto the preparative column, was eluted from the column over the course of about 40 min, and was fractioned as described as follows.

General extract screening analysis

The first test sample was analyzed by liquid chromatography coupled with ultraviolet and mass spectrometry (LC/UV/MS). The general chromatographic conditions were as follows:

Column	Phenomenex (Torrance, CA) Prodigy C8, 150 × 4.6 mm, 5-μm particles
Mobile phase	Component A, 40/60 methanol/water, 0.1% formic acid. Component B, acetonitrile
Flow rate	0.7 mL/min
Column temperature	30°C
Detection	MS; API-ES, positive ion mode, 105–1500 amu mass range. UV at 230 nm

Gradient:

Time (min)	Proportion A
0.0	100
1.0	100
20.0	10
30.0	10
31.0	100

Sample size 100 μL

Extract fractionation

The second sample was fractionated by preparative LC. The general chromatographic conditions were as follows:

Column	Phenomenex Prodigy C8, 250 × 21.2 mm, 5-μm particles
Mobile phase	Component A, 40/60 methanol/water, 0.1% formic acid. Component B, acetonitrile

Gradient:

Time (min)	Proportion A
0.0	100
1.0	100
20.0	10
40.0	10

Flow rate	15 mL/min; split after separation with 14.4 mL/min going to fractionation tubes and the remainder going to the analytical detector
Detection	UV (230 nm) and MS (positive ion mode)
Sample loading	Sample was loaded onto the preparative column by multiple injections made before the initiation of the elution gradient

Chromatographic fractions were collected in the following manner. For the first sample portion, fractions were collected every minute, after an appropriate delay to allow for elution of the system void. For the remaining sample portion, fractions were collected manually on a peak-to-peak basis (at ~ 1-min intervals).

Fraction analysis

The collected fractions were evaporated to a minimal volume to remove the organic volatiles of the mobile phase leaving an aqueous solution. The volume reduced samples were then lyophilized to produce a solid sample for structural analysis.

Portions of the solid fractions were analyzed in several ways. Some of the material was resolubilized and injected into an analytical LC/MS system so that the compounds in the fractions could specifically be correlated with peaks observed in LC/MS chromatograms associated with the direct analysis of material extracts. Another portion of the material was analyzed by NMR and a third portion was analyzed by advanced MS techniques to provide accurate mass and MS/MS fragmentation spectra.

The NMR testing proceeded as follows. The test materials were dissolved in $CDCl_3$. In all cases the test material dissolved rapidly and completely. The resulting solutions were transferred to individual 5-mm NMR sample holder tubes and examined without further modification. In one case a test material was

dissolved originally in a mixture of CD_3CN/D_2O. After preliminary analysis, the solvent was removed under a stream of $N_2(g)$ and the resulting solid was redissolved in $CDCl_3$.

Test solutions were examined using Avance DRX600 NMR and DRX400 spectrometers (Bruker Instruments, Billerica, MA). The following NMR experiments were performed: one-dimensional (1D) proton (^1H) spectrometry, 1D carbon-13 (^{13}C) spectrometry, two-dimensional (2D) $^1H/^1H$ correlation spectrometry (COSY), 2D $^1H/^1H$ total correlation spectrometry (TOCSY), 2D diffusion-order spectrometry (DOSY), 2D $^1H/^{13}C$ heteronuclear multiple-quantum correlation (HMQC) spectrometry, and 2D $^1H/^{13}C$ heteronuclear multiple-bond correlation (HMBC) spectrometry. All chemical shifts were referenced by a method equivalent to defining $CHCl_3$ as δ7.24 ppm. Chemical shifts were obtained from the video-display terminal, using the screen cursor. Relative peak areas were obtained from the height of classic line-trace integrals, measured in constant arbitrary units.

MS/MS and accurate mass MS experiments were carried out using collected HPLC fractions. The HPLC fractions were taken to dryness under a stream of nitrogen. The residue was then dissolved in either 0.1% TFA/acetonitrile (50 : 50) or 10 mM ammonium acetate in 90% acetonitrile. The resulting solution was loaded into a nano-spray sample capillary and analyzed on a Micromass® Q-Tof Micro™ mass spectrometer (Waters, Milford, MA). For accurate mass measurements, either 1-tetradecylamine or resperpine was used as the internal standard for mass calibration.

General instrument parameters were as follows: capillary voltage: 800–1000 V, cone voltage: 35–50 V, source block temperature: 80°C, collision energy: 4.0 V (no MS/MS experiments), desolvation gas: 50 L/h, and nanoflow gas: 2 psi. For MS/MS, Ar was used as the collision gas and the collision cell pressure was approximately 20 psi.

Compound accumulation in solution

Extraction

Test articles were prepared by extracting 10 g of nylon-6 resin with 100 mL of extracting solvent. The three extracting solvents used were 0.1*N* HCl (low pH), water (unbuffered), and 0.01*M* phosphate buffer, pH 9 (high pH). One set of test articles per solution type was extracted by storage at 70°C for 72 h or at 121°C for 1 h (autoclaving). Subsequently, the test articles were stored at ambient temperature for about 6 months. In this way, a contact situation of autoclaving followed by an extended period of ambient temperature storage, as is typical in pharmaceutical applications, was simulated. Duplicate test samples were prepared for each extracting solution/extraction temperature couple and extraction controls (extracting solution in extraction vessel with no resin) were prepared and stored alongside the test articles. The extraction vessels were 100-mL Pyrex® glass bottles.

Extract analysis

The nylon-6 extracts were analyzed by LC/UV/MS by a methodology that was similar to that used for the scouting experiment. Some method optimization was performed to improve the quantitative aspects of the original assay. The general chromatographic conditions were as follows:

Column	Phenomenex Prodigy C8, 150 × 4.6 mm, 5-μm particles
Mobile phase	Component A, 40/60 methanol/water, 0.1% formic acid. Component B, acetonitrile
Flow rate	0.7 mL/min
Column temperature	30°C
Detection	MS; API-ES, positive ion mode. Extracted diagnostic $[M + H^+]$ ions from the MS total ion current (TIC) chromatograms for quantitation. Ions used included (in amu) caprolactam, 114; dimer, 227; trimer, 340; tetramer, 353; pentamer, 566; hexamer, 679. UV at 230 nm (used for scouting but not for quantitation)
Sample size	100 μL

Gradient:

Time (min)	Proportion A
0.0	100
1.0	100
20.0	10
28.0	10
29.0	100
31.0	100

Quantitation of the individual oligomers was accomplished as follows. Authentic references materials for caprolactam and its dimer and pentamer were available and were used to prepare standards. Analysis of the standards allowed for the calculation of response factors (peak area/analyte concentration in the standard). The concentrations of caprolactam monomer, dimer, and pentamer in the extracts and controls were directly calculated as the product of the compound's response factor and the compound's peak response in the samples. Because no authentic reference material was available

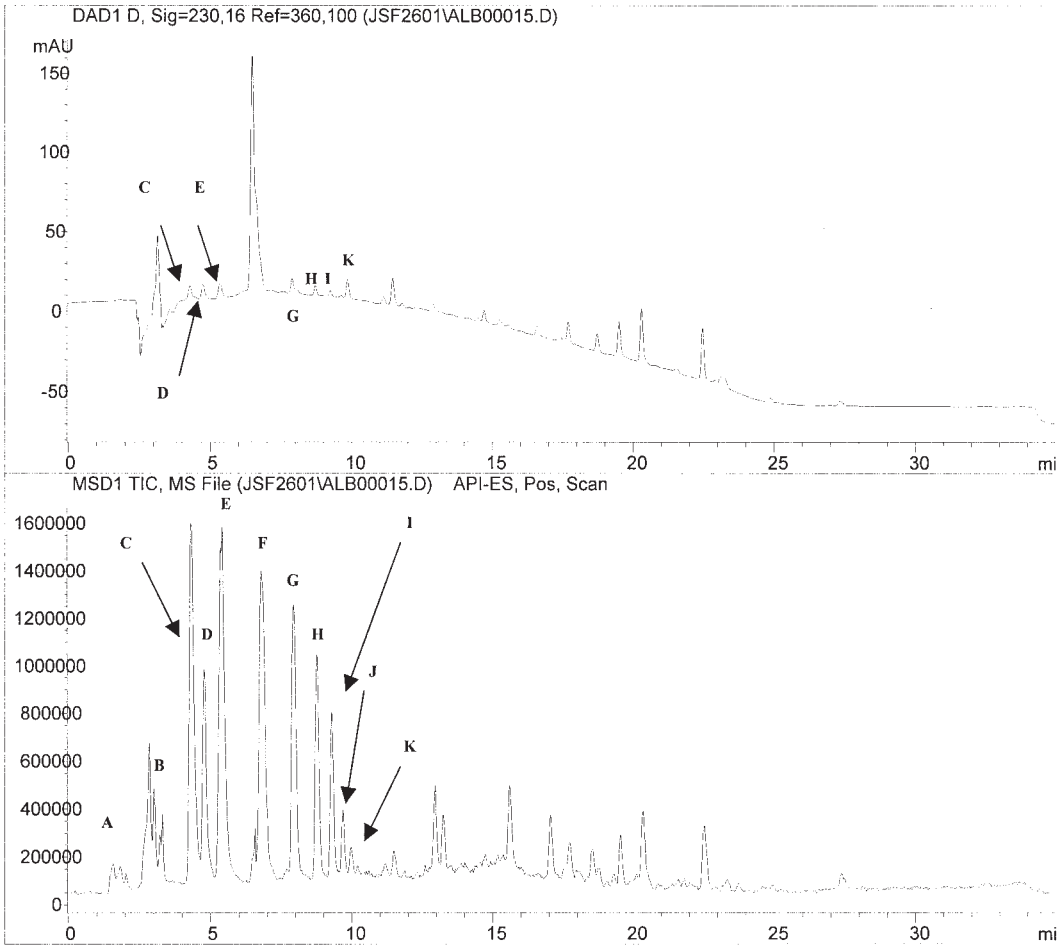


Figure 1 UV (230 nm) and MS (TIC) chromatograms of an ethanol–water extract of the polyolefin laminate film. See Table I for peak identifications, relevant for caprolactam and its oligomers. (Although the chromatogram contains peaks related to compounds other than caprolactam and its oligomers, evaluation of such peaks was outside the scope of this study.)

for the other oligomers (trimer, tetramer, hexamer, heptamer), the concentrations of these compounds were estimated as the product of the mean response factor for the monomer, dimer, and pentamer and the compound's response in the samples.

Chromatographic instrumentation

The quantitative analysis of the nylon-6 extracts and controls was performed using an 1100 HPLC system (pump, autosampler, column oven; Agilent, Palo Alto, CA) coupled to an MDS SCIEX API 4000 mass detector (Applied Biosystems, Toronto, Canada). The preparative separations were performed with a Dynamax Prep LC System (Rainin, Woburn, MA) with SD-1 pumps and UV-D-2 UV detector.

RESULTS AND DISCUSSION

Compound isolation and identification

General extract screening

The MS total ion current (TIC, positive ionization mode) and UV (230 nm) chromatograms from this experiment are shown in Figure 1. The chromatograms are complex, exhibiting more than 20 peaks of sufficient response to warrant investigation. Analyses performed using the negative ion mode produced similar chromatographic profiles that contained the same peaks (and only the same peaks) that were observed in the positive ion chromatograms.

The chromatograms were examined in two ways. Each individual peak in the TIC and UV chromatograms was characterized with respect to its associated MS ions. Additionally, extracted ion chromatograms (EICs) were generated at each specific mass/charge (m/z) ratio between 105 and 1500 amu and examined for the presence of peaks. The resulting data were used to generate tentative identifications for numerous peaks in the sample chromatograms. Not all the peaks observed were investigated because the total number of peaks was large; rather, those responses of the largest size were afforded the greatest attention. A compilation of the relevant peaks observed in Figure 1 is contained in Table I. The tentative identifications contained in this table reflect potential members of the

TABLE I
Peak IDs, Chromatograms of an Ethanol/Water Extract of the Polyolefin Materials (Fig. 1)

Peak label	Retention time (min)	Compound identification	Diagnostics ions (m/z)
A	2.7	Caprolactam hydrolyzed dimer	245
B	2.9	Caprolactam hydrolyzed trimer	340, 358
C	4.3	Caprolactam dimer	227, 249
D	4.8	Caprolactam monomer	114, 136
E	5.4	Caprolactam trimer	340
F	7.1	Caprolactam tetramer	453, 475
G	8.1	Caprolactam pentamer	566, 588
H	8.8	Caprolactam hexamer	340, 679, 701
I	9.3	Caprolactam heptamer	396, 792, 814
J	9.6	Caprolactam octamer	163, 453, 905, 927
K	10.0	Caprolactam nonamer	510, 1040

polyolefin's extractables survey and included an entire series of caprolactam-related oligomers (n = 1 to 9 observed) as well as numerous other compounds whose identification is not germane to this article.

The chromatogram contains several peaks whose associated compound could not be identified based on the data available from this experiment. Most of these peaks are discernibly smaller than the peaks associated with identified compounds, suggesting that their concentrations are low.

Extract fractionation and fraction analysis

The tentative identifications obtained in the chromatographic screening were confirmed by sample fractionation and comprehensive fraction characterization. These identifications were based on structural and compositional information afforded by information-rich analytical methods such as accurate mass MS (provides the unique molecular formula and accurate formula weight of the compound), MS/MS (provides functional associations by defining a compound's fragmentation pattern), and NMR (provides structural information related to C/H connectivity). The data supporting a compound's identification and the identification rationale are contained in the Appendix.

Compound accumulation

The concentrations of caprolactam and its related cyclic oligomers in the aqueous extracts of the nylon-6 resin are summarized in Table II. The concentrations of these compounds were very reproducible from sample to sample and were not materially affected by

TABLE II
Levels of Caprolactam and Its Oligomers in Nylon-6 Extracts

			Concentration in extract, (ppm)						
Solution	Rep. no.	T (°C)	Monomer	Dimer	Trimer	Tetramer	Pentamer	Hexamer	Heptamer
0.1*N* HCl	1	70[a]	3.9	6.0	28.2	23.2	10.7	2.0	0.3
	2	70	3.8	5.9	27.4	21.6	10.7	2.0	0.2
	3	121[b]	4.5	6.2	27.9	23.1	12.2	3.3	0.7
	4	121	4.3	6.0	27.2	21.7	11.8	3.1	0.5
	Blank	70	0.2	0.7	4.1	2.8	0.6	0.0	0.0
	Blank	121	0.0	0.1	0.5	0.2	0.0	0.0	0.0
Water	7	70	30.3	8.0	29.1	25.8	12.3	2.2	0.2
	8	70	28.6	8.3	28.5	24.0	11.2	2.2	0.2
	9	121	23.9	8.5	27.4	26.6	13.3	3.7	1.0
	10	121	28.2	8.1	30.2	25.3	14.0	3.6	1.0
	Blank	70	0.2	0.1	0.6	0.5	0.1	0.0	0.0
	Blank	121	1.9	0.8	5.2	4.1	0.8	0.1	0.0
Buffer, pH 9.1	13	70	29.4	7.9	28.5	24.3	11.6	2.1	0.2
	14	70	28.1	8.5	29.1	23.5	12.2	2.2	0.3
	15	121	27.2	8.9	28.1	26.5	14.3	3.6	0.9
	16	121	27.6	7.1	29.3	24.7	13.6	3.7	0.8
	Blank	70	0.9	0.0	0.1	0.0	0.0	0.0	0.0
	Blank	121	0.3	0.0	0.1	0.0	0.0	0.0	0.0

[a] For 72 h.
[b] For 1 h.

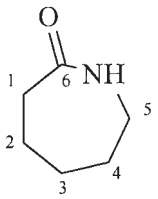
the initial (high temperature) extraction conditions. The effect of extracting solution pH on the compound's concentration in the extract is small, except for the monomer, whose accumulation is significantly decreased at low pH. Much smaller decreases in the levels of the dimer, tetramer, and pentamer were also observed in the acidic extract.

Oligomers up to $n = 5$ were present at high and comparable levels in all the nylon-6 extracts. The levels of the oligomers dropped off rapidly with increased compound size after $n = 5$, with the heptamer being minimally observable in the extracted ion chromatogram. None of the extracted ion chromatograms had peaks for oligomers greater than $n = 6$. This distribution of oligomers in the commercially available nylon-6 material is clearly different from the oligomer distribution in the nylon layer of the multilaminate film, as evidenced by the difference in the relative oligomer proportions shown in Figure 1 (nylon from film) versus the proportion shown in Table II (commercially available material). Because the oligomer distribution is impacted by numerous material processing parameters, this difference is not unexpected.

APPENDIX:

ANALYTICAL DATA AND STRUCTURAL INFORMATION OF THE IDENTIFIED COMPOUNDS.

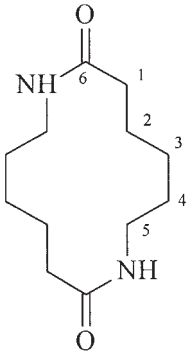
A. Caprolactam; 2H-Azepin-2-one, hexahydro- [105-60-2]. $C_6H_{11}NO$; formula weight, 113.14; C = 63.69%, H = 9.80%, N = 12.38% O = 14.14%.



600 MHz NMR results		
Atom label	^{1}H ppm (multiplicity)	^{13}C ppm
1	2.476	36.17
2	1.680	23.39
3	1.812	30.50
4	1.648	29.62
5	3.233	42.38
6	Carbonyl group	180.76

Accurate mass results					
Mass	Calculated mass	mDa	PPM	DBE	Formula
114.0912	114.0919	−0.7	−6.0	1.5	$C_6H_{12}NO$
114.0944	114.0919	2.5	22.0	1.5	$C_6H_{12}NO$

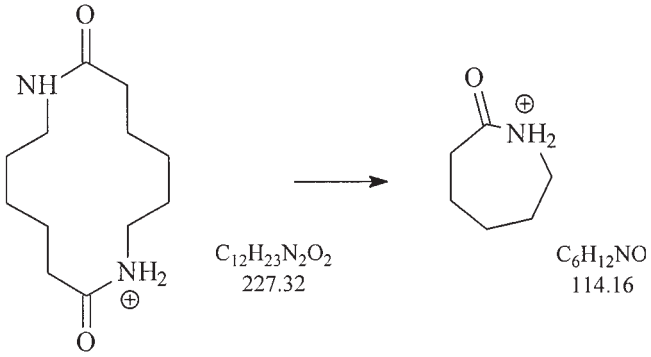
B. Caprolactam Cyclic Dimer: 1,8-Diazacyclotetradecane-2,9-dione [56403-09-9]. $C_{12}H_{22}N_2O_2$; formula weight, 226.31; C = 63.69%, H = 9.80%, N = 12.38% O = 14.14%.



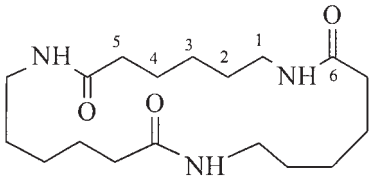
600 MHz NMR results		
Atom label	^{1}H ppm (multiplicity)	^{13}C ppm
1	2.210	35.58
2	1.648	25.55
3	1.329	25.29
4	1.503	29.02
5	3.276	38.53
6	Carbonyl group	175.11

Accurate mass results					
Mass	Calculated mass	mDa	PPM	DBE	Formula
227.1733	227.1760	−2.7	−11.7	2.5	$C_{12}H_{23}N_2O_2$
249.1539	249.1579	−4.0	−16.0	2.5	$C_{12}H_{22}N_2O_2Na$
227.1757	227.1760	−0.3	−1.1	2.5	$C_{12}H_{23}N_2O_2$

MS/MS Fragmentation: 227.1858, 209.1781, 114.0960, 96.0869
Structural Reconciliation of Fragmentation Pattern:



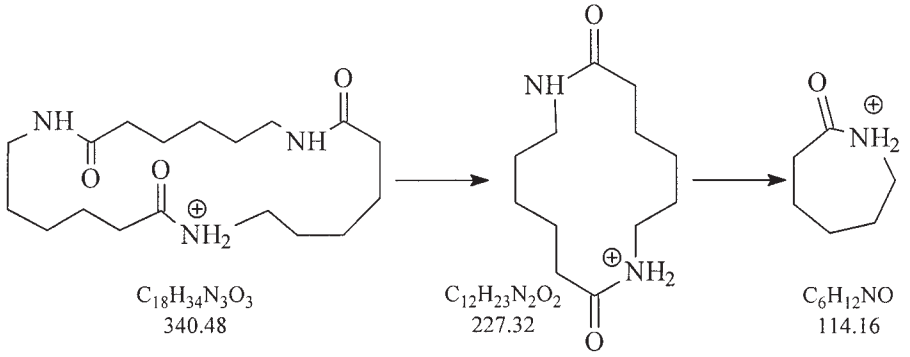
C. Caprolactam Cyclic Trimer: 1,8,15-Triazacycloheneicosane-2,9,16-trione [56403-08-8]. $C_{18}H_{33}N_3O_3$; formula weight, 339.47; C = 63.69%, H = 9.80%, N = 12.38% O = 14.14%.



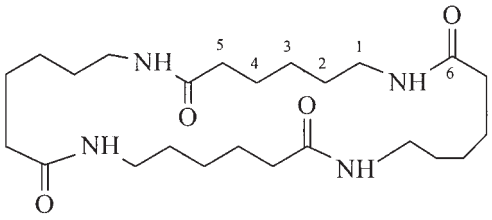
600 MHz NMR results		
Atom label	^{1}H ppm (multiplicity)	^{13}C ppm
1	2.212	35.65
2	1.650	25.25
3	1.355	25.89
4	1.540	28.62
5	3.203	38.90
6	Carbonyl group	175.10

Accurate mass results					
Mass	Calculated mass	mDa	PPM	DBE	Formula
340.2603	340.2600	0.3	0.8	3.5	$C_{18}H_{33}N_3O_3$
362.2399	362.2420	−2.1	−5.7	3.5	$C_{18}H_{33}N_3O_3Na$
340.2585	340.2600	−1.5	−4.5	3.5	$C_{18}H_{34}N_3O_3$

MS/MS Fragmentation: 340.2777, 322.2710, 227.1858, 209.1781, 114.0960 (From Standard Compound)
Structural Reconciliation of Fragmentation Pattern:



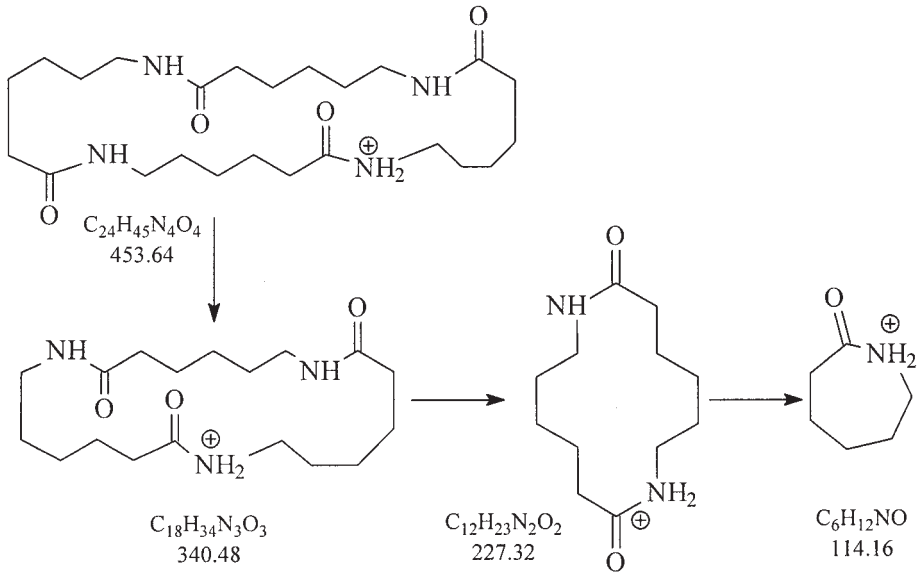
D. Caprolactam Cyclic Tetramer: 1,8,15,22-Tetraazacyclooctacosane-2,9,16,23-tetrone [5834-63-9]. $C_{24}H_{44}N_4O_4$; formula weight, 452.63; C = 63.69%, H = 9.80%, N = 12.38% O = 14.14%.



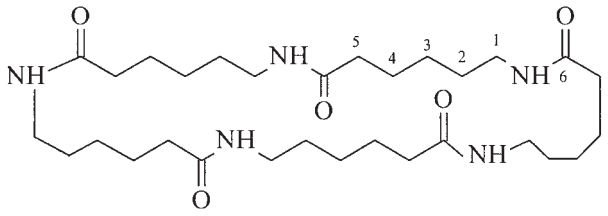
600 MHz NMR results		
Atom label	^{1}H ppm (multiplicity)	^{13}C ppm
1	2.206	35.89
2	1.643	25.58
3	1.346	26.28
4	1.532	29.04
5	3.197	39.06
6	Carbonyl group	174.97

Accurate mass results					
Mass	Calculated mass	mDa	PPM	DBE	Formula
453.3423	453.3441	−1.8	−3.9	−4.5	$C_{24}H_{45}N_4O_4$

MS/MS Fragmentation: 453.3656, 435.3436, 340.2812, 322.2737, 226.2067, 209.1747, 114.1022
Structural Reconciliation of Fragmentation Pattern:



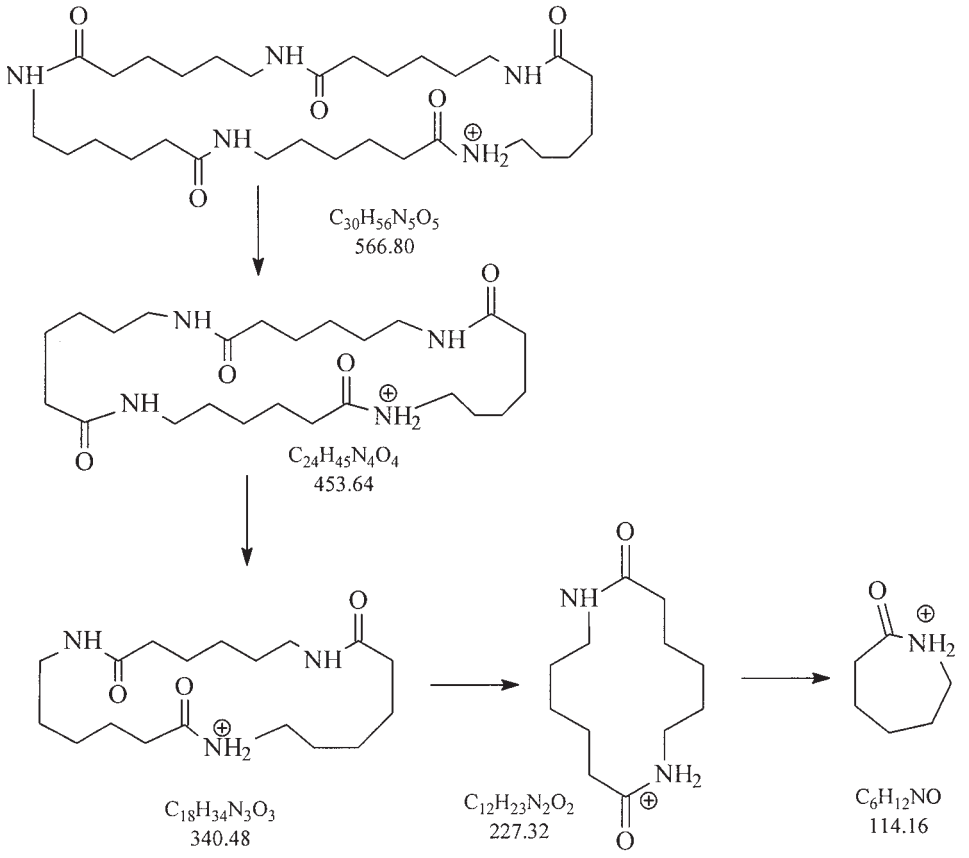
E. Caprolactam Cyclic Pentamer: 1,8,15,22,29-Pentaazacyclopentatriacontane-2,9,16,23,30-pentone [864-90- 4]. $C_{30}H_{55}N_5O_5$; formula weight, 565.79; C = 63.69%, H = 9.80%, N = 12.38% O = 14.14%.



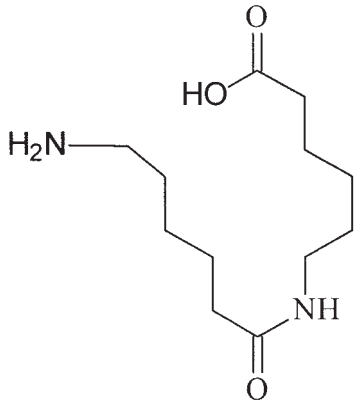
600 MHz NMR results		
Atom label	^{1}H ppm (multiplicity)	^{13}C ppm
1	2.199	35.97
2	1.641	25.69
3	1.349	26.41
4	1.532	29.09
5	3.189	39.10
6	Carbonyl group	174.97

Accurate mass results					
Mass	Calculated mass	mDa	PPM	DBE	Formula
566.4283	566.4281	0.2	0.3	5.5	$C_{30}H_{56}N_5O_5$

MS/MS Fragmentation: 566.4750, 548.4605, 453.3907, 435.3682, 340, 322.2737, 227, 209.1917, 114.1148. Structural Reconciliation of Fragmentation Pattern:



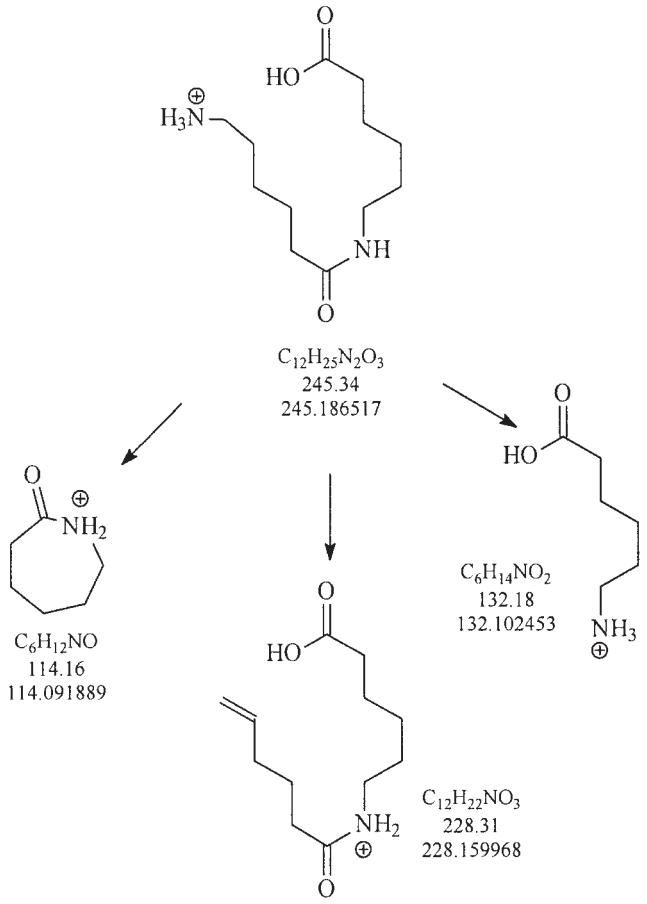
F. Hydrolyzed Caprolactam Dimer: Hexanoic acid, 6-[(6-amino-1-oxohexyl)amino]- [2014-58-6]. $C_{12}H_{24}N_2O_3$; formula weight, 244.33; C = 58.99%, H = 9.90%, N = 11.47% O = 19.64%.



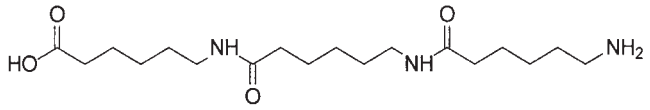
600 MHz NMR results		
Atom label	^{1}H ppm (multiplicity)	^{13}C ppm
Not performed		

Accurate mass results					
Mass	Calculated mass	mDa	PPM	DBE	Formula
245.1870	245.1865	0.5	2.0	1.5	$C_{12}H_{25}N_2O_3$

MS/MS Fragmentation: 245.1967, 228.1626, 227.1838, 132.1085, 114.0898
Structural Reconciliation of Fragmentation Pattern:



G. Hydrolyzed Caprolactam Trimer: Hexanoic acid, 6-[[6-[(6-amino-1-oxohexyl)amino]-1-oxohexyl]amino]- [5776-78-3]. $C_{18}H_{35}N_3O_4$; formula weight, 357.49; C = 60.48%, H = 9.87%, N = 11.75% O = 17.90%.

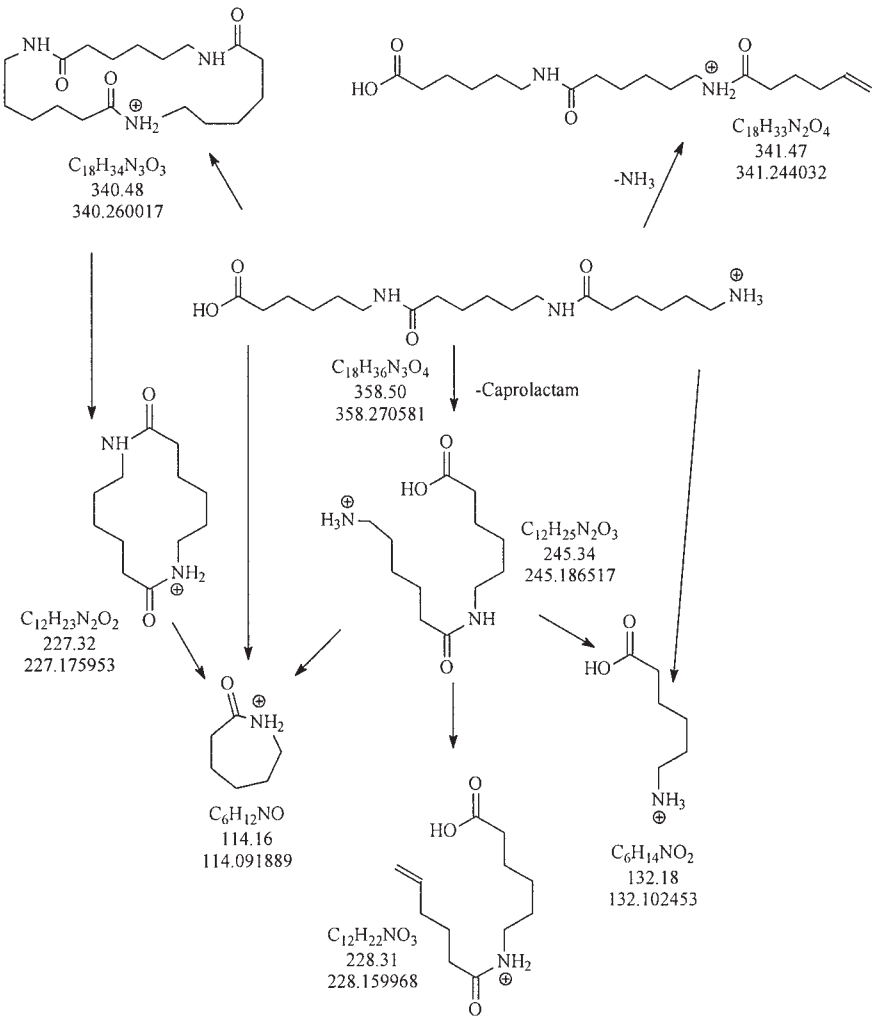


600 MHz NMR results		
Atom label	^{1}H ppm (multiplicity)	^{13}C ppm
Not performed		

Accurate mass results					
Mass	Calculated mass	mDa	PPM	DBE	Formula
358.2681	358.2706	−2.5	−6.9	2.5	$C_{18}H_{36}N_3O_4$

MS/MS Fragmentation: 358.2638, 341.2386, 340.2590, 322.2523, 245.1967, 228.1626, 227.1838, 209.1752, 132.1085, 114.0898

Structural Reconciliation of Fragmentation Pattern:



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