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Short communication

# Supercritical fluid extraction of nylon 6,6 oligomers and their characterization via liquid chromatography coupled with mass spectrometry

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**Abstract**

This research extends previous studies regarding the application of supercritical fluid extraction (SFE) for the analysis of oligomers from nylon 6,6 fibers. The effects of $CO_2$ pressure, extraction temperature, $CO_2$-modifier percentage, static extraction time and dynamic extraction time on the SFE efficiency of nylon 6,6 oligomers were examined. Results from the SFE methods for oligomer extractions were compared to results from conventional solvent extraction. The extracted oligomers were identified by high-performance liquid chromatography (HPLC) with coupled on-line atmospheric pressure chemical ionization mass spectrometry and HPLC fractionation coupled with off-line liquid secondary ion mass spectrometry. 

*Keywords:* Supercritical fluid extraction; Nylon 6,6

## 1. Introduction

The quantitation of the amount of low-molecular-mass material present in polymeric fibers is an important industrial quality control practice. If the quantity of low-molecular-mass species is too large, they tend to deposit as a white powder on processing equipment, resulting in mechanical error [1]. In addition to the effect of high oligomer concentrations on the processing of fibers, broad polymer size distributions lead to less desirable fiber properties [2].

Several researchers have studied the extraction of low-molecular-mass oligomeric material from polymeric matrices with supercritical $CO_2$. Küppers [3] was able to selectively extract low-molecular-mass components from PET using supercritical fluid extraction (SFE). In this study, a selective two-step extraction was used, whereby oligomers were first removed from the outside of the fibers and then from the fiber core. Bartle et al. [4] also studied the SFE of oligomers from PET films. Off-line SFE/supercritical fluid chromatography (SFC) with 100% $CO_2$ at 70°C and 400 atm was carried out. They found that the cyclic trimer was the main component of the extracts, but that the extractions were not exhaustive, even after 13 consecutive 30 min extractions. Soxhlet extractions with *p*-xylene as the solvent were

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performed for comparison to the SFE data [5]. Material extracted with *p*-xylene Soxhlet extraction was determined gravimetrically. SF extracts were analyzed by capillary SFC.

Venema and van de Ven [6] extracted caprolactam and other oligomers from nylon 6 via SFE. The influence of particle size, extraction time and methanol modifier on the extraction efficiency were examined. They found that the addition of methanol during the static step followed by dynamic extraction with 100% $CO_2$ resulted in complete extraction of caprolactam, even for large particle sizes. The extraction of higher oligomers, however, required the presence of methanol during both the static and dynamic steps. It was also determined that a larger quantity of oligomers was removed with the SFE method than with methanol Soxhlet extraction.

Lou et al. [7] performed a systematic study for the removal of oligomers from nylon 6 and poly(1,4-butyleneterephthalate) (PBT). In these experiments, dichloromethane liquid trapping was employed followed by evaporation of the solvent and re-dissolution of the residue in chloroform for gas chromatography–flame ionization detection (GC/FID) analysis. Methanol was the most effective modifier for extracting nylon 6, whereas chloroform was a better modifier for extraction of PBT. Further experiments indicated that the amounts of caprolactam from nylon 6 and dimer from PBT removed with SFE were equivalent to the amounts obtained with methanol and chloroform Soxhlet extraction, respectively.

Jordan and Taylor [8] studied the use of a SFE–SFC–FT-IR system for the identification and quantification of oligomeric materials from nylon. For the extraction of caprolactam from a nylon 6,6/nylon 6 copolymer, four different traps were examined to determine trapping conditions for maximum recovery of caprolactam. They found that methyl- and cyano-coated silica capillary traps yielded higher caprolactam recoveries and higher precision than stainless steel or bare silica.

In this study, efforts have been made to analyze low-molecular-mass oligomers in nylon 6,6 fibers using SFE. The investigation concerned the effects of various extraction parameters on extraction efficiency followed by quantitation of the extracted oligomer with high performance liquid chromatography (HPLC). The final goal of the research was to identify all extracted oligomers via mass spectroscopy.

## 2. Experimental

Bulk continuous filament (BCF) nylon fiber samples of 1200 denier were obtained from Dupont (Chattanooga, TN, USA). The fibers were coated with a finish containing tropical and vegetable oils, a potassium salt and an ethylene–propylene oxide derivative. For quantitation of residual monomer in the bulk fiber, off-line SFE with HPLC was used. A standard of a single, raw oligomer was purified by recrystallization with ethyl acetate. For the LC portion of the analyses, a Hewlett-Packard series 1050 HPLC was used with the following parameters:

Column: 250×4.6 mm Phenomenex Prodigy ODS(III), 5 μm particle size
UV detector, 214 nm
Mobile phase, isocratic 70/30 (v/v) $H_2O$/MeOH
Flow-rate, 1 ml/min
Injection volume, 20 μl
Analysis time, 10 min

All solvents were of HPLC grade and were obtained from Fisher Scientific (Fair Lawn, NJ, USA). The ratio of aqueous to organic portions of the mobile phase was chosen as needed to yield a capacity factor ($k'$) of two for the oligomer.

Quantitation of the oligomer was accomplished by using an external calibration curve. To generate this curve, a 500-ppm stock standard oligomer solution in methanol was made and successively diluted twice with methanol to encompass oligomer concentrations of 0 to 500 ppm. Each standard was analyzed three times using the LC conditions stated above. A correlation coefficient of 0.9995 was obtained for the calibration.

An initial spike study was performed to determine the solubility of the oligomer in both pure and modified $CO_2$. In these experiments, samples were prepared in which 200 μl of a 500-ppm stock oligomer solution was spiked onto Ottawa sand (Fisher Scientific) contained in 1 ml extraction vessels. The solution was allowed to dry under atmospheric conditions for several hours. The samples were then extracted with the following conditions:

Extraction fluid, 100% $CO_2$ or 90:10 (v/v) $CO_2$–$CH_3OH$
Pressure, 350 atm
Oven temperature, 75°C
Dynamic extraction time, 20 min
Restrictor temperature, 75°C
Solid phase trap, ODS at 75°C
Flow-rate, 1.5 ml/min
Trap desorption temperature, 30°C
Trap rinse: twice, each with 1.5 ml methanol

Both rinses per extraction were analyzed, but the analyte was always contained in the first rinse. Experiments using both types of extraction fluids were performed in triplicate. For extraction of the oligomer from the bulk fiber, 50 mg fiber samples that had been previously extracted with 100% $CO_2$ for finish removal were placed into 1 ml extraction vessels. The small sample size was used in order to conserve sample and to avoid overloading the solid-phase trap with extractables.

Conventional liquid–solid extractions with 55:45 (v/v) heptane–methanol (as prescribed by the industry) were performed for comparison to the SFE results. In this procedure, 50 mg of fiber were placed into a 25-ml Erlenmeyer flask and 11 and 9 ml of heptane and methanol were added to it, respectively. The mixture was stirred for 1 h, following which, the fibers were removed and rinsed with an additional 3 ml of methanol. The solvent was then evaporated down to about 2 to 3 ml under a stream of purified nitrogen. The remaining solvent was then added to a 5-ml volumetric flask, and methanol was added to make a total volume of 5 ml. The sample was then analyzed by HPLC–UV.

A Hewlett-Packard series 1050 HPLC and a Micromass Platform/MS with atmospheric pressure chemical ionization (APCI) were employed. The main parameters used were as follows:

LC
Column, Prodigy ODS(III) 250×4.6 mm (Phenomenex)
Mobile phase, 60:40 (v/v) $H_2O$–MeOH; isocratic sample solvent, methanol
Flow-rate, 1 ml/min
Injection volume, 10 μl (partially filled loop)
MS
Probe temperature, 400°C
Source temperature, 120°C
Cone voltage, 30 V
Gain, 3
Mass range, 100–1000 amu

For analyses involving direct insertion with LSIMS ionization, a Fisons VG quattro mass spectrometer (Manchester, UK) with a cesium ion beam was used in the single quadrupole mode. A droplet of glycerol on the probe tip was used to hold the sample. In order to concentrate each sample, a few microliters of sample in a water–methanol solution were placed onto the glycerol on the probe tip, and then the tip was placed in a vacuum to evaporate the solvent. Following this, a few additional microliters of sample were placed onto the glycerol and the probe was inserted through the vacuum lock into the spectrometer. The main mass spectral parameters used were as follows:

Ionization mode, FB+
Liquid matrix, glycerol
Cesium beam voltage, 50 kV
FAB probe temperature, 20°C
Cycle time, 10 s/scan
Mass range, 100 to 1000 amu

The FB+ ionization mode refers to ionization by fast atom bombardment (FAB) or LSIMS in positive-ion mode.

## 3. Results and discussion

Our goal was to analyze for the oligomers that could be extracted from the polymer bulk with supercritical fluids. The samples that were available for our study contained a surface finish. Our strategy was to first extract finish components with 100% $CO_2$ and then extract bulk oligomer with modified $CO_2$. Unfortunately, low-molecular-mass oligomer was found to be soluble in pure supercritical $CO_2$. Therefore, some oligomer (~100 μg/g of extracted fiber) was extracted along with all of the finish components via 100% $CO_2$. This amount was deemed to be insignificant compared to what could be extracted with modified $CO_2$. For extraction of oligomer from the bulk finish-free fiber, the effects of temperature, pressure, static and dynamic time, spike volume and the percentage of methanol modifier were investigated.

Increasing the extraction temperature from 40 to

75°C at constant pressure leads to a statistically higher oligomer extraction recovery. This effect is common in the extraction of a polymer since higher temperatures increase the diffusivity of the extraction fluid, allowing more efficient penetration into the amorphous phase of the matrix. Also, since the $T_g$ of nylon 6,6 ranges from −7 to 108°C, higher temperatures increase the likelihood of extracting above the $T_g$ of the polymer. Extraction pressure and, therefore, the density, of the fluid, however, was not a critical parameter in the extraction of the oligomer. In other words, recovery was essentially the same at 300, 350 and 400 atm.

The addition of a static step into the extraction conditions did not have any effect on the recovery of oligomer from pre-extracted fiber. The addition of 250 μl of methanol to the vessel prior to a 10-min static step, however, yielded a statistically greater amount of extracted oligomer compared to samples extracted with no spike. The methanol present during the static step may aid in swelling the amorphous phase of the polymer, thus allowing for quick extraction of the analyte during the dynamic step. The addition of a small amount of in-line methanol modifier to the $CO_2$ rather than the matrix during the dynamic step was also found to aid in extraction. This was expected, since nylon 6,6 possesses polar amide functional groups. The extraction conditions chosen for removal of bulk oligomer were therefore:

| | |
|---|---|
| Pressure, 400 atm | Flow-rate, 1.5 ml/min |
| Temperature, 100°C | Restrictor temperature, 75°C |
| Modifier, 10% MeOH (v/v) | Spike volume, 250 μl |
| Trap, ODS at 75°C | Trap desorption temperature, 30°C |
| Static time, 10 min | Dynamic time, 15 min |
| Trap rinse, twice, each with 1.5 ml of MeOH | |

The trap was flushed twice following each ex-

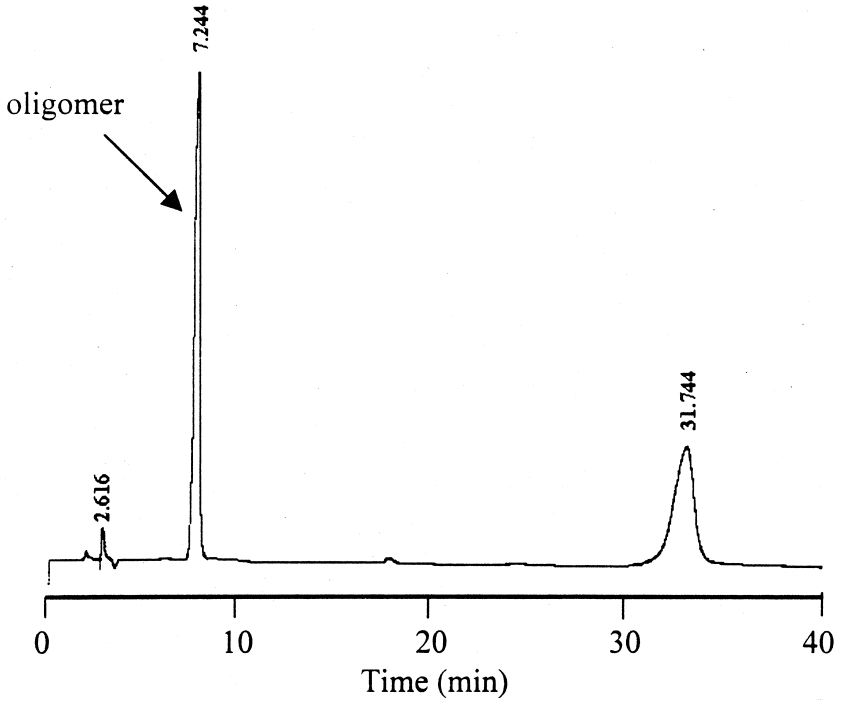


Fig. 1. Oligomer chromatogram with extended run time LC conditions: 250×4.6 mm Phenomenex prodigy ODS (III) column with 5 μm particle size, 70:30 (v/v) $H_2O$–$CH_3OH$, 20 μl injection volume, 1 ml/min flow-rate, 214 nm UV detection.

traction and both rinses were analyzed, but the analyte was always contained in the first rinse.

For comparison to the SFE data, conventional solvent extractions using 55:45 (v/v) heptane–methanol were also performed. The results of the extraction of oligomer from the pre-extracted fiber using SFE (6460 μg) and liquid–solid (3670 μg) extraction at room temperature were quite different. Each value represents at least three data points. The low RSDs obtained with SFE (4.5 vs. 11.7%) indicated that using small sample sizes did not cause a reproducibility problem in this technique. Higher precision was obtained with the SFE method, probably due to the fewer number of steps and, therefore, the reduction in sample handling compared to solvent extraction.

As previously stated, a much larger quantity of oligomer was extracted from the fiber sample with SFE than with the organic solvent mixture. After 1 h of soaking the fiber in heptane–methanol, oligomer continued to be removed. This is in sharp contrast to SFE where the monomer is completely removed in 10 min of dynamic extraction. This could be due to greater diffusion of $CO_2$–methanol into the matrix at the higher temperature of the SFE, as opposed to the lower temperature liquid–solid extraction. When the heptane–methanol extraction was performed at 50°C, the amount of oligomer extracted was equivalent to the SFE results after 20 min extraction.

Since the SFE method had successfully removed one oligomer, it seemed logical that other oligomers might be removed as well. In this regard, when the HPLC analysis for monomer was extended for a longer time period, additional peaks were observed in the chromatograms of both SF and liquid extracts (Fig. 1). It was hypothesized that these extra peaks were higher oligomers, but appropriate standards were not available for retention time comparisons to be made.

In order to identify the species giving rise to these chromatographic peaks, mass spectrometry (e.g. APCI mode) was coupled with HPLC. The mass spectrum obtained via HPLC–APCI–MS of peak 1 from the separation of the supercritical extract is

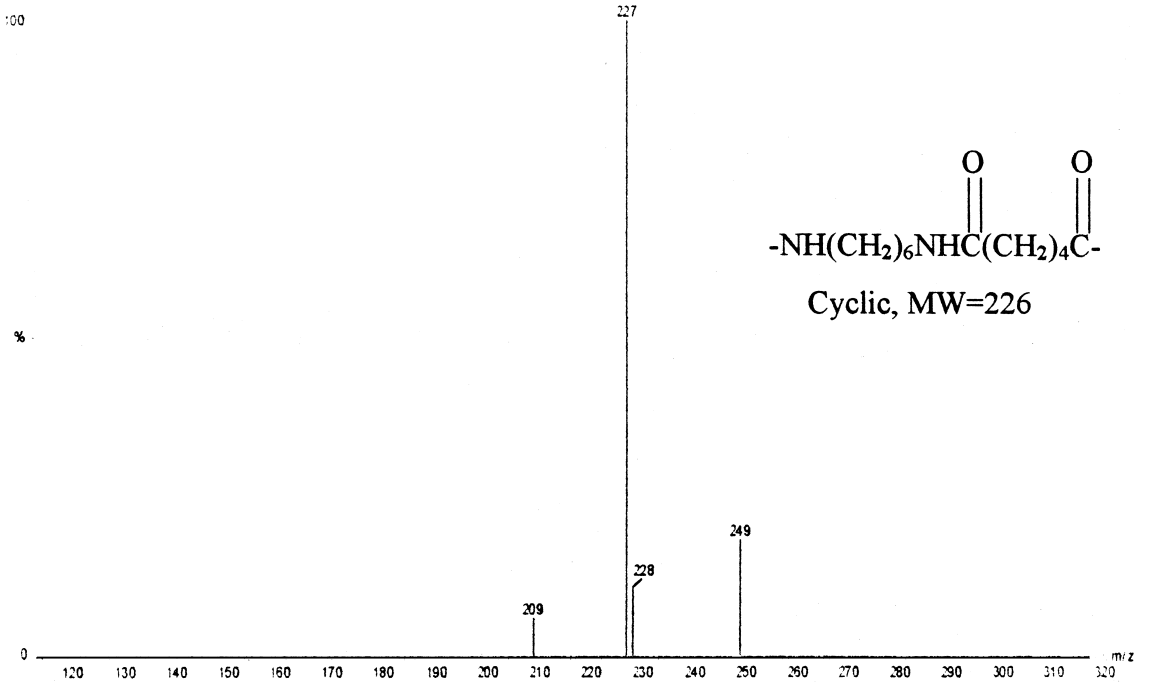


Fig. 2. LC–APCI–MS spectrum of 50 ppm oligomer standard. LC conditions: Phenomenex Prodigy ODS (III) 250×4.6 mm column with 5 μm particle size, 70:30 $H_2O$–MeOH isocratic, 10 μl injection volume, 1.5 ml/min flow-rate. MS conditions: Ionization, APCI; 400°C probe; 120°C source; cone voltage, 30 V; gain, 3.

Table 1
Various nylon 6,6 oligomers

| Oligomer | Molecular mass |
|---|---|
| Cyclic monomer (A–C) | 226 |
| Cyclic dimer | 452 |
| H–A–C–A–H monomer* | 342 |
| H–A–C–A–H dimer* | 455 |
| H–A–C–A–H trimer* | 795 |
| H–C–A–C–H monomer* | 372 |
| H–C–A–C–H dimer* | 598 |
| H–C–A–C–H trimer* | 825 |
| H–A–C–H monomer* | 244 |
| H–A–C–H dimer* | 470 |
| H–A–C–H trimer* | 697 |

shown in Fig. 2. The spectra of the peak 1 component and the oligomer standard were similar, with a base peak at 227 amu.

A list of known oligomers of nylon 6,6, which was obtained from DuPont, is presented in Table 1. The cyclic monomer has a molecular mass of 226, so it is possible that this peak from both oligomer standard and SF extract contained the cyclic monomer as the $(M+H)^+$ species. The ion at 209 in the spectrum of the standard could indicate loss of water. The reason for the occurrence of the 249 ion in both spectra is unknown.

*A-H = -NH-$(CH_2)_6$-$NH_2$- MW = 115

*C-H = HO-C-$(CH_2)_4$-C- MW = 129

*A = -N-$(CH_2)_6$-$NH_2$- MW = 114

*C = -C-$(CH_2)_4$-C- MW = 112

In order to confirm the results obtained with LC–APCI–MS, HPLC fractions (off-line) of each peak from a supercritical fluid extract were obtained and analyzed by direct insertion LSIMS. In order to determine the background ions caused by the glycerol matrix, the spectrum of pure glycerol was obtained. Ions of $m/z$ 93, 185, 277, 369, etc. are common in the glycerol spectrum and represent $(\text{glycerol}_n)H^+$ ions. The base peak appears to occur at 227 amu, which confirms the results obtained by

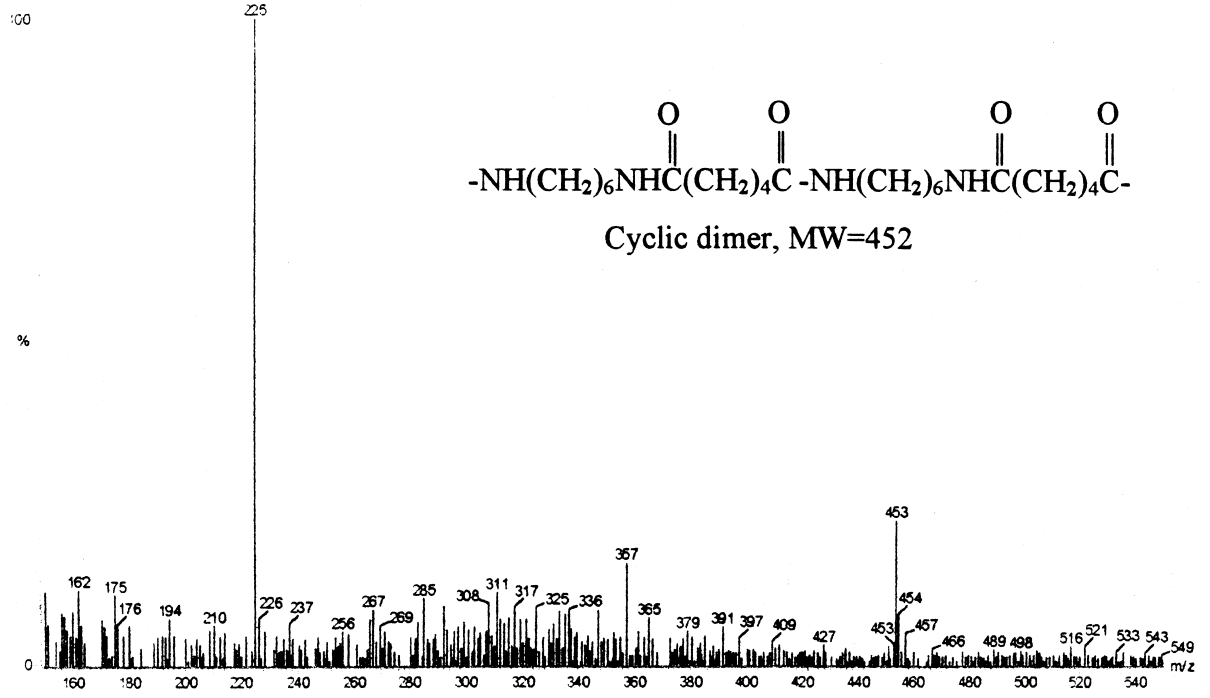


Fig. 3. LSIMS spectrum of peak 2 with the glycerol spectrum removed.

LC–APCI–MS, which indicated that this oligomer is likely to be the cyclic monomer. However, there are many more ions present in the LSIMS spectrum than in the APCI–MS spectrum of this peak. This was expected since the formation of adducts between the analyte and the glycerol matrix is extremely common. [9] The ion at 183 amu (loss of 44 amu) could possibly represent the loss of $NH_2C=O$.

Since the LSIMS determination of peak 1 was successful, an attempt was made to identify the remaining peaks in the chromatogram using this technique as well. Fig. 3 depicts the spectrum of peak 2 with the glycerol spectrum removed. Here, a major ion is found at 453 amu, which could correspond to the cyclic dimer. The identification of peaks 3 and 4 was not as successful using the MS technique. The spectra of both peaks contained a 225 ion, however, no ions corresponding to higher known oligomers of nylon 6,6 were found in either spectrum.

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