Supercritical Fluid Extraction of Nylon 6,6 Fiber Finish and Oligomers

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Thesis submitted to the Faculty of the Virginia Polytechnic Institute and State University in partial fulfillment of the requirements for the degree of

Master of Science

in

Chemistry

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December 1997

Blacksburg, Virginia

Keywords: Supercritical Fluid Extraction, SFE, Fiber Finishes, Oligomers, Nylon 6,6, HPLC, Mass Spectrometry

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(ABSTRACT)

Quantitation of the amount of finish applied during fiber manufacturing is an important industrial quality control process. Finish levels that are too low result in excessive fiber and mechanical wear. On the other hand, overly high finish levels may cause residue buildup on the processing equipment. Removal of the finish has traditionally been done with solvents such as chloroform or Freon followed by gravimetric or spectroscopic analysis of the removed material.

Quantitation of low molecular weight oligomeric material is another important quality control practice for the fiber industry in that the presence of these species and their concentration affect the physical properties of the polymer. Also, excessively high concentrations of oligomers may result in residue deposits on processing equipment. Typical conventional methods for determining the concentration of oligomers present in fibers involve large quantities of organic solvent for removal of the oligomers followed by chromatographic analysis.

Increased government regulation of chlorinated and other solvents has led to investigations of alternate methods of extraction. Several studies have shown that supercritical fluid extraction (SFE) using carbon dioxide as the extraction fluid is an important alternative to conventional organic solvent extraction for the removal of both textile finishes and oligomeric material. This research seeks to extend the previous studies regarding the application of SFE for the quantitation of finish and 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 supercritical fluid extraction efficiency of nylon 6,6 oligomers were examined. Results from the SFE methods for both finish and oligomer extractions were compared to results from conventional solvent extraction. The extracted oligomers were identified by HPLC with coupled on-line atmospheric pressure chemical ionization mass spectrometry (APCI-MS)

and HPLC fractionation coupled with off-line Liquid Secondary Ion Mass Spectrometry (LSIMS).

Acknowledgements

I would like to express my gratitude to all that provided friendship and support and gave so freely of their time during my stay at Virginia Tech. In particular, thanks to Dr. Larry Taylor for his guidance and for his confidence in me, it was an honor and a privilege to be part of his research group. To all fellow and former members of the Taylor group, in particular: Dr. Michael Combs, Dr. Mehdi Ashraf-Khorassani, Dr. Rose Shi, Susan Smith, Angela Pinto, Lori McDaniel, Phyllis Eckard, Lucy Zhou and Dan Brannegan, thank you for providing invaluable advice for this study and for helping to make working in the lab more enjoyable. To my committee, Dr. Taylor, Dr. John Dillard, and Dr. Harry Dorn, thank you for the advice that you have given and for taking the time to serve as my committee members. Fred Blair in the physics machine shop also deserves thanks for fixing many of my mechanical mistakes. Thank you to Kim Harich in Analytical Services for his assistance in obtaining the mass spectra. Gratitude is also expressed to Dr. Paul Seemuth and the Dupont Corporation (Chattanooga, TN) for providing samples and financial support for this project, and to Air Products and Chemicals Inc. (Allentown, PA) for donating the carbon dioxide used in the supercritical fluid extractions. Also, I wish to acknowledge my parents, David and Alvera Risch, as well as my other family members, George, Sandra, Erin, Alex, Sonny, Donna, and Jennifer, for their constant prayers and many votes of confidence. Last, but not least, I thank God for my husband David Porter, who has been my source of stability and comfort during the rough stages and who has been the first to celebrate with me all of the victories, large and small.

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Chapter 1

Introduction

Nylon 6,6 Fibers

Nylon 6,6 is a polyamide formed from the condensation (step growth) polymerization of hexamethylene diamine and adipic acid at elevated temperature and pressure, as shown in Figure 1. The 6,6 nomenclature stems from the six carbon units on both the amine and acid starting materials. In a step growth reaction, multifunctional monomers successively combine with another monomer to form a dimer, which in turn combines with another dimer, and so forth. This is in contrast to an addition (chain growth) polymerization, in which a long molecular chain grows from unsaturated monomer units, followed by growth of a second chain, and so forth. Nylon 6, another polyamide commonly made into fibers, is formed by addition (1).

Following polymerization, the reaction pressure is reduced to allow the removal of water of condensation, and after drying, the nylon 6,6 is extruded. Following this, the polymer is typically pelletized and/or melt spun into fibers (1,2). The degree of polymerization of nylon 6,6, or the average number of monomer repeat units in a chain, ranges from 100 to 250 units. The degree of crystallinity of the polymer fiber is dependent on the level of orientation brought about by drawing (1). The glass transition (T_g) of nylon 6,6 ranges from about –8°C to approximately 107°C, depending on the relative humidity of its environment. The melting temperature, (T_m) is about 250°C. Nylon 6,6 is most commonly used in fiber form for construction of textile materials, such as carpeting, upholstery, hosiery, and weatherproof outerwear. Items such as parachutes and sails are also commonly made from nylon 6,6 fibers (1,3).

Textile Fiber Finishes

Textile fiber finishes exist primarily to facilitate the processing of natural and man made fibers. The actual composition of a particular finish depends on the type of fiber to be manufactured as well as processing conditions for the fiber. Typical finishes may

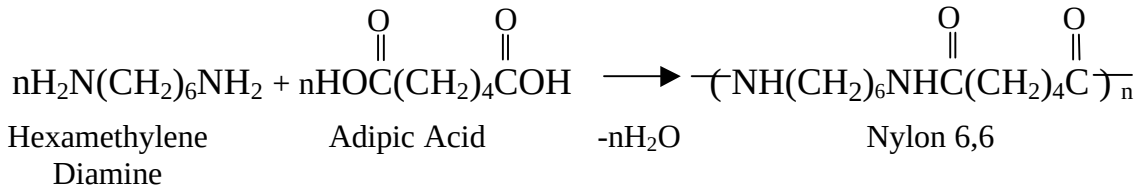

Figure 1. General synthesis for nylon 6,6

contain one or more lubricants, anti-static agents, cohesive agents, emulsifiers, anti-bacterial agents, and/or other compounds. Lubricants such as vegetable oils and hydrocarbon waxes reduce the coefficient of friction between the fibers and the processing equipment, decreasing fiber and mechanical wear. Anti-static agents dissipate static charges between the fibers themselves and between the fibers and manufacturing equipment that tend to appear during processing. Cohesive agents are often present to form the individual fibers into a fiber bundle, thus allowing for easier processing and handling. It is convenient to apply the finish as an aqueous base, so emulsifiers are also typically incorporated into the finish. In addition to the above components, small amounts of antioxidants and/or anti-bacterial agents are sometimes added to the finish blend to prevent the finish itself from decomposing or undergoing microbial attack (3).

Quantitation of the amount of applied finish is an important quality control process in fiber manufacturing. Finish levels that are too low result in excessive fiber and mechanical wear, but on the other hand, finish levels that are too high may result in finish buildup and fiber adhesion on processing equipment. The main portion of a typical finish is largely comprised of oil blends, so quantitation of finish level has traditionally involved removal of the finish with non-polar solvents such as Freon, chloroform, or carbon tetrachloride, followed by spectroscopic measurement of the extracted finish in solution or gravimetric analysis of the extracted residue (4). In recent years other means of finish determination have been investigated due to increasing concern over chlorinated and other common extraction solvents as environmental and health hazards (9-15).

Supercritical Fluid Extraction

Critical temperature and pressure, as shown in Figure 2, define what is termed the critical point of a substance. The critical pressure is defined as the maximum pressure at which a liquid can be converted to a gas by an increase in temperature. The critical temperature is analogous to the critical pressure in that it is the maximum temperature at which a gas can be converted to a liquid by an increase in pressure. Above the critical

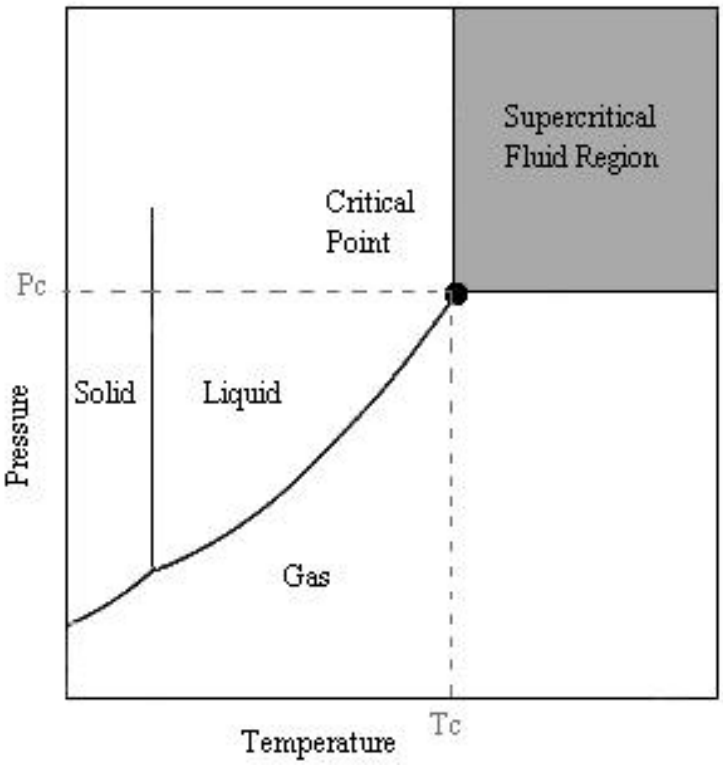

Figure 2. Phase Diagram for a single component

point the supercritical fluid region is found, where a single phase exists that has properties intermediate between those of gases and liquids. The physical properties of a typical gas, liquid, and supercritical fluid (SCF) are compared in Table I. As seen in the Table, the density of the SCF is closer to that of a liquid, but the density and viscosity of the fluid are closer to that of a gas. These properties make the SCF very useful as a solvent. The high density gives the SCF solvating power similar to a liquid, but the high diffusivity and low viscosity (as well as near zero surface tension) allow it to penetrate into difficult matrices and remove analytes with efficiency similar to that of a gas (5,6).

By far the most common fluid used in supercritical fluid extraction (SFE) is carbon dioxide. The critical parameters of CO_2 are about 31°C and 73 atm, conditions that are easily attained in the laboratory. Critical parameters of other common fluids used in SFE are shown in Table II. Carbon dioxide is readily available in pure form, and is environmentally friendly and non-toxic, things that have become of greater concern in recent years due to increasing governmental regulation of hazardous materials (7).

A schematic illustrating the main components of a supercritical fluid extraction system is shown in Figure 3. A gas cylinder provides a source of CO_2, which is pumped into the system with either a piston or syringe type pump. For the experiments described in this thesis, a SFE system with a piston pump was employed. Piston pumps are more convenient when using modified fluids, in that it is easier to change modifiers without system contamination from the previous solvent. Piston pumps also allow continuous addition of fluid into the system, whereas a fixed amount of fluid is available from a syringe pump. Therefore, more samples may be analyzed consecutively with a piston pump.

A supplementary modifier pump is used if the analyte/matrix to be extracted requires an extraction fluid that is more polar than carbon dioxide alone. The sample to be extracted is placed into the extraction vessel, which is in turn placed inside a thermostatically controlled oven heated above the critical temperature of the extraction fluid. The restrictor is one of the most important parts of an extraction system, in that it maintains back pressure in the system so that supercritical conditions are maintained, and

Table I. Physical Data for Gas, Supercritical Fluid, and Liquid States (taken from ref. 5)

	Density (g/mL)	**Dynamic Viscosity** (g/cm-sec)	**Diffusion Coefficient** (cm^2/sec)
Gas (ambient)	0.0006-0.002	0.0001-0.003	0.1-0.4
Supercritical Fluid (Tc, Pc)	0.2-0.5	0.0001-0.0003	0.0007
Liquid (ambient)	0.6-1.6	0.002-0.03	0.000002

Table II. Critical parameters of common fluids used for SFE (taken from ref. 5)

Gas	**T_C (°C)**	**P_C (bar)**
Xenon	16.6	57.6
Trifluoromethane	25.9	46.9
Chlorotrifluoromethane	29.0	38.7
Carbon dioxide	31.0	72.9
Dinitrogen monoxide	36.5	71.7
Sulfur hexafluoride	45.5	37.1
Chlorodifluoromethane	96.4	48.5
Propane	96.8	42.4
Ammonia	132.4	111.3
Trichlorofluoromethane	198.0	43.5
Water	374.0	217.7

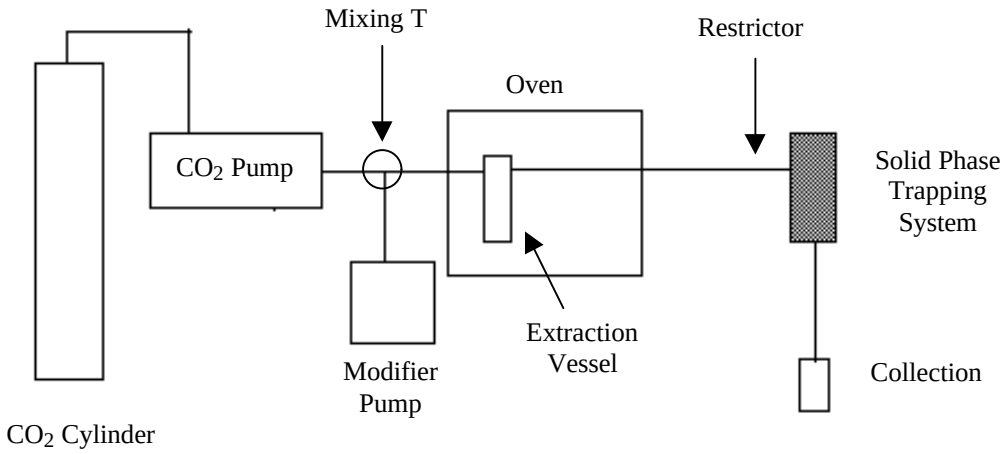

Figure 3. Block diagram of SFE system

it serves as the interface between the high pressure cell and the laboratory atmosphere. Following the restrictor is a trapping system; the most common of which solid phase and liquid solvent. Common solid phases are chromatography column packings such as octadecyl silica (ODS), solid sorbents such as Tenax™ and graphite, or inert surfaces such as glass wool and glass or stainless steel beads. The solid phase trapping systems are often heated or cooled depending on the volatility of the extracted analytes. If liquid trapping is desired, the restrictor outlet is immersed directly into a solvent such as methanol, methylene chloride, or other solvent. The solvent is chosen so that the extracted analyte will remain solvated in the trapping liquid (5).

The two principal modes of supercritical fluid extraction are static and dynamic. In a static extraction, the sample matrix is exposed to a fixed amount of CO_2. This type of extraction is often compared to a teabag in a cup of water. A dynamic extraction, in contrast, continuously passes fresh CO_2 through the sample matrix. This situation is analogous to coffee grounds in a modern coffee maker. Many SFE methods employ a combination of both static and dynamic modes; a static mode is used to allow the CO_2 to penetrate the matrix and solubilize the analyte(s), followed by a dynamic mode which sweeps the analytes from the vessel, through the restrictor, and into the trap. Once the CO_2/analyte has passed through the restrictor, the CO_2 decompresses to atmospheric pressure and loses the bulk of its solvating power. The analyte therefore precipitates into the trap. If a solid phase trap is used, a supplementary rinsing pump is often employed to rinse the analytes from the trap into a collection device.

In most cases, many parameters must be investigated to develop a quantitative extraction method that yields the highest efficiency. The extraction pressure is an important variable in that the pressure is directly related to the density and hence the solvating power of the extraction fluid. Also of great importance is the extraction temperature. The higher the temperature, the greater the diffusivity of the fluid. Higher temperatures may also increase the sublimation pressure of an analyte, aiding in extraction. However, high temperatures are not always advantageous in that an increase in temperature may result in a reduction in fluid density, and therefore the solvating

power is reduced. For these reasons, assessment of the appropriate temperature and pressure parameters may determine the success or failure of an analytical supercritical fluid extraction (5).

Difficult matrices such as a polymeric matrix require special considerations when developing a SFE method. The extraction temperature is critical when removing analytes from a polymer. A general rule of thumb for extraction from a semi-crystalline polymer is that the temperature should be above the glass transition temperature (T_g) but below the melting temperature (T_m). A temperature above the T_g results in enough molecular motion in the amorphous phase of the polymer so that the CO_2 can diffuse into the region easily. However, a temperature below the T_m is critical so that the crystalline phase of the polymer does not melt, clog the extraction system and possibly ruin the extraction vessel.

Also of importance in the SFE of a polymer is determining if the addition of a co-solvent, or modifier, is necessary. Addition of a modifier is a particularly common practice if the polymer incorporates polar functional groups as part of its structure. A modifier may swell the amorphous phase of the polymer, allowing the CO_2 to diffuse into the region more easily. Depending on the polarity of the analyte to be extracted, the modifier may also solubilize the analyte to a greater extent than the essentially non-polar carbon dioxide itself. Modifier can be incorporated directly into the matrix or mixed with the CO_2 fluid (8,9). When a modifier is incorporated into the fluid, the critical temperature and pressure (Tc and Pc) may be estimated from the following equation:

$$Tc = X_{CO2}Tc_{(CO2)} + X_mTc_{(m)} \qquad \text{Equation 1}$$

$$Pc = X_{CO2}Tc_{(CO2)} + X_mTc_{(m)} \qquad \text{Equation 2}$$

where X_{CO2} and X_m are the mole fractions of the CO_2 and modifier, respectively and $Tc_{(CO2)}$, $Pc_{(CO2)}$, $Tc_{(m)}$, and $Pc_{(m)}$ are the critical parameters of the CO_2 and modifier alone (10). More rigorous calculation of the critical parameters of mixtures are described elsewhere (11,12).

Fiber Finish Analysis

Supercritical fluid extraction methods for finish level quantitation have been widely investigated. Yocklovitch, et al. (13) performed one of the first studies in which a coupled supercritical fluid chromatography/supercritical fluid extraction (SFE/SFC) system was used to compare fiber samples for quality control purposes. The researchers found that the amount of extracted material detected was directly proportional to the extracted sample size. In this study, a separation of a finish blend containing solvents, vegetable oil triglycerides, and alkyl ethoxylates was also obtained.

Drews, et al. (14) were able to extract finishes from polyethylene terephthalate (PET), nylon, and polypropylene fibers with supercritical carbon dioxide. Finish quantitation was obtained by gravimetric sample weight loss as well as gravimetric finish recovery. The SFE temperature chosen was based on the boiling point of a corresponding Soxhlet extraction solvent. Extraction pressure was chosen by determining a density of carbon dioxide that had a Hildebrand solubility parameter equivalent to that of a corresponding soxhlet solvent at its boiling point. The researchers found that for PET, the SFE method duplicated results from Soxhlet extraction with 1,1,1 trichloroethylene. However, the amount of finish removed from nylon fibers with supercritical CO_2 was 0.1 to 0.2% less than that obtained from Soxhlet extractions with petroleum ether. The SFE method also removed significantly less material from the polypropylene fibers than did Freon Soxhlet extractions. At the time of this study, it was unknown if the reason for the discrepancy between SFE and Soxhlet extraction was due to an inability of the SFE method to remove all of the finish components, or if the SFE method was removing less oligomeric material than the Soxhlet extractions.

In a further study by Drews, et al. (15), investigations were carried out to determine the validity of basing SFE conditions on the boiling point and Hildebrand solubility parameter of corresponding solvents for soxhlet extraction. Finish was extracted from PET yarn, polypropylene fiber, as well as several fabric samples. Temperature and pressure effects on the amount of finish extracted from the materials were studied. The researchers found that the appropriate SFE temperature and pressure windows were wider than expected. However, at higher temperatures more oligomeric material was extracted from the fiber.

Höfler and Alt (16) performed a study in which open tubular SFC was used to separate common finish components such as polysiloxanes, ethoxylates of fatty alcohols, and hydrocarbon waxes. The authors found that SFC with 100% CO_2 could be used to separate hydrocarbon waxes up to a carbon number of C120 at a column temperature of 120ºC. They also found that polysiloxanes up to a polymerization degree of n>80 could be analyzed by this method. In an additional study, coatings from yarn and sewing thread were analyzed directly with on-line SFE/SFC. Since the coating mixture was complex, several peaks were identified, but baseline separation was not achieved.

Kirschner, et al. (17) investigated the feasibility of finish extraction and quantitation with an on-line SFE/FT-IR system. Polyurethane, polyamide, and aramid fibers were analyzed. From off-line SFE studies, it was found that the polurethane finish was the most easily extracted, and that the polyamide and aramid finish recoveries were lower due to lower solubility of certain finish components in supercritical CO_2. However, the recoveries of finish were high enough to extract and analyze by SFC/FT-IR. The researchers found that the flow rate was critical in direct static/dynamic SFE/FT-IR, in that it needed to be fast enough to extract quickly, but not so fast as to create excessive noise in the FT-IR signal. Quantitation was accomplished for polyamide and aramid finish with Gram-Schmidt reconstruction, however this method could not be used directly for quantitation of the polyurethane finish due to the presence of co-extractives. Therefore, a plot of the IR signal for a finish selective frequency region was used for quantitation of the polyurethane finish, and a limit of detection of 3.7 μg was obtained.

When the SFE/FT-IR extraction results were compared to standard extraction with tetrachloroethylene, a lower amount of finish was obtained with the SFE method, probably due to the additional extraction of low molecular weight oligomers with the solvent method.

Jordan and Taylor (18) extended the notion of using SFE/FT-IR for the extraction and quantitation of fiber finishes to include intermediate trapping. A complex finish for polyester fibers was examined. They found that a static period with a dynamic period that had a slow enough flow rate to avoid excessive noise was not sufficiently exhaustive to quantitate the finish level. This problem was overcome with the use of intermediate trapping, which allowed the use of faster flows for quicker dynamic extraction. Sample transfer and IR collection from the trap was accomplished in 2-3 minutes. The amount of finish was obtained using the 1120-1100 cm-1 region due to a large absorbance from a single, highly extractable component. The limit of detection was 0.65 μg. The data were comparable to solvent extraction with tetrachloroethylene.

Liescheski, et al. (19) coupled SFE with IR using a high pressure flow cell that fits most commercial IR or FT-IR equipment. This system was used for quality control analysis of a polyurethane finish, polydimethylsiloxane. They found that a 10 mm flow cell was too long for this application, in that higher finish concentrations tended to saturate the IR absorbance signal at certain bands. To overcome this limitation, small sample sizes and a weakly absorbing band were used for quantitation. Similar results were obtained for the SFE/IR method when compared to both liquid extraction with infrared analysis as well as gravimetric SFE.

SFE of Oligomeric Material from Polymers

IUPAC defines oligomers as species that exhibit changes in their behavior when one or more repeat units are added or removed (20). Since significant changes do not occur in polymers in this situation, oligomers may be thought of as the low molecular weight analogues of polymers (21). The quantitation of the amount of low molecular weight material present in polymeric fibers is another important industrial quality control

practice. If the quantity of low molecular weight species is too large, they tend to deposit as a white powder on processing equipment, resulting in mechanical error (3). In addition to the effect of high oligomer concentrations on the processing of fibers, broad polymer size distributions lead to less desirable fiber properties (1).

Several researchers have studied the extraction of low molecular weight oligomeric material from polymeric matrices with supercritical CO_2. Küppers (22) was able to selectively extract low molecular weight components from PET using 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. The extracts were qualitatively analyzed by gas or liquid chromatography. A systematic study of optimum parameters for oligomer extraction was also performed, and the amount of material extracted increased with both increased pressure and increased density. The use of modified CO_2 was also investigated, and the researchers discovered that dichloromethane modified CO_2 increased the amounts of extracted oligomers, but that methanol and isopropyl alcohol as CO_2 modifiers prevented oligomers from being extracted.

Bartle, et al. (23) derived a model for diffusion limited extraction which has been termed the "hot-ball" model in which the amount of an analyte from a short supercritical fluid extraction may be mathematically extrapolated to yield the actual amount present in the starting matrix. Several assumptions were made in this model, namely, that the particles in the matrix are spheres, that the analyte is uniformly distributed through the matrix, and that the concentration of the analyte in the supercritical fluid is effectively zero. It is appropriate to apply this model to polymeric materials due to the fact that extractions of these materials are often diffusion limited.

Bartle, et al. (24) applied this basic model with some additional modifications to the SFE of oligomers from PET films. Both off-line and on-line SFE/SFC with 100% CO_2 at 70°C and 400 atm were carried out. In the off-line experiments, 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. Using the hot ball model, a calculated value for a 6.5 hour extraction compared favorably with the actual

experimental results. On-line extractions gave inconsistent results due to the fact that the long extraction times required to correctly fit the extraction model were impractical.

Cotton, et al. (25) also studied the supercritical fluid extraction of oligomers from PET. Their research was concerned primarily with determining the rate and extent of cyclic trimer extraction from the polymer. Soxhlet extractions with p-xylene as the solvent were performed for comparison to the SFE data. Material extracted with p-xylene soxhlet extraction was determined gravimetrically. SF extracts were analyzed by capillary SFC. Extraction pressure was set at 400 atm, and the temperature was varied to study the effect it had on the extractability of the trimer. Higher temperatures were found to increase the amount of analyte extracted, which was consistent with a diffusion limited extraction. The authors used the hot-ball model described by Bartle et al. for diffusion limited extractions to predict the initial concentration of cyclic trimer species in the PET from a short time supercritical fluid extraction. After interpreting the data from a 30 minute extraction using this model, they found that the result yielded the same amount of analyte as an actual 2 hour extraction. This value was less than that obtained from liquid extraction, but the difference was attributed to the presence of residual solvent in the liquid extract.

Venema and van de Ven (26) 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 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. (9) 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 GC/FID analysis. It was found that

the effectiveness of modifiers added directly to the extraction cell was matrix dependent; methanol was the most effective modifier for extracting nylon 6, whereas chloroform was a better modifier for extracting PBT. It was also found that the modifiers were more effective at lower temperatures. 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. However, the recovery of trimer from PBT was lower with SFE than with chloroform soxhlet extraction. The authors indicated that the use of continuous modifier addition, rather than just addition to the extraction cell at the beginning of SFE, may increase the recovery of the PBT trimer.

Jordan and Taylor (27) studied the use of a SFE/SFC/FT-IR system for the identification and quantification of oligomeric materials from nylon and polystyrene. 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. The addition of methanol modifier to the extraction vessel greatly enhanced the recovery of the analyte, most likely due to swelling of the polymer which allowed the caprolactam to rapidly diffuse to the surface. In additional experiments, low molecular weight oligomers were extracted from polystyrene using the SFE/SFC/FT-IR system. It was found that the use of a C18 column and a cyano column in tandem yielded the best separation of the oligomers. Higher temperatures at constant density resulted in higher recoveries of oligomers. Extracted species were identified via on line FT-IR detection, wherein cyclic and linear oligomers were differentiated.

In this thesis, efforts have been made to quantify the amounts of finish and low molecular weight oligomers in Nylon 6,6 fibers using supercritical fluid extraction. The introductory portion of the work involved removal of the finish from the surface of the fibers via SFE with 100% CO_2 followed by conventional gravimetric analysis. The second part was an investigation of the effects of various extraction parameters on the

extraction efficiency of a low molecular weight nylon 6,6 oligomer, followed by quantitation of the oligomer with high performance liquid chromatography (HPLC). The goal of the third section of the research was to identify all extracted oligomers via mass spectroscopy.

A secondary goal of this effort was to determine if the extraction methods could discern the origin of white residues that a certain fiber sample deposited on processing equipment. In the following discussion, this sample will be referred to as the "problem" fiber sample. Two control fiber samples were also analyzed for comparison; these will be referred to as "control (1)" and "control (2)".

Chapter 2

Quantitative Extraction of Nylon 6,6 Fiber Finish

Introduction

Supercritical fluid extraction followed by gravimetric analysis was used as an alternative method to conventional chloroform extraction for the removal of nylon 6,6 fiber finish. The results from the two extractions were statistically compared using F as well as t tests. The purpose of the F test was to compare the precision of two data sets using the following equation:

$$F_{calc} = \frac{S_{x1}^{\ 2}}{S_{x2}^{\ 2}} \qquad \text{(Equation 3)}$$

Where S_{x1} and S_{x2} are the standard deviations of each data set.

A calculated t value from the following equation was used to determine if two different methods provided equivalent data.

$$t_{calc} = \frac{\left|\bar{x}_1 - \bar{x}_2\right|}{Sp\sqrt{\frac{1}{n_1} + \frac{1}{n_2}}} \qquad \text{(Equation 4)}$$

The values x_1 and x_2 are the average values of each of the two data sets, Sp is the pooled standard deviation, and n_1 and n_2 are the number of data points in each set. Both calculated F and calculated t values were compared to F and T values from standard tables at the 99% confidence level (28).

The main objective of these introductory experiments was to obtain equivalent results for both methods, and to determine if the “problem” fiber sample was coated with a large excess of finish as compared to the “control” samples.

Experimental

Bulk continuous filament (BCF) nylon fiber samples (2 control samples and 1 problem sample) of 1200 denier were obtained from The Dupont Co. (Chattanooga, TN). The fibers were coated with a finish containing tropical and vegetable oils, a potassium salt, and an ethylene/propylene oxide derivative. For the determination of percent finish on yarn (%FOY), the supercritical fluid extraction conditions developed previously by Kirschner and Jordan for this fiber type were used (14). Fiber samples were extracted as received. An Isco/Suprex (Lincoln, NE) AP44 automated extraction system equipped with an automatic variable restrictor and Accutrap™ collection system was used with the following conditions:

Extraction fluid: 100 % CO_2	Extraction vessel size: 5 mL
Oven temperature: 75 °C	Liquid flow rate: 1.5 mL/min
Pressure: 350 Atm	Liquid trap: 7 mL CH_2Cl_2
Restrictor temperature: 75 °C	Trap rinse: 1.5 mL CH_2Cl_2

Several changes were made to the previously optimized method, which included an increase in sample size from 50 mg to 750 mg in order to allow gravimetric analysis of the extracts, and the use of the Suprex AP44 instead of the Suprex MPS-225. Liquid trapping was accomplished by attaching a piece of stainless steel tubing to the restrictor block outlet and placing the end of the tubing into a test tube containing methylene chloride. The 1.5 mL methylene chloride rinse was used to rinse the stainless steel line directly into the collection solvent following extraction.

The optimum dynamic time was determined by the finish extraction profile shown in Figure 4. The extraction profile was obtained by performing six consecutive 10 min extractions, with a change of collection solvent between each extraction. Following extraction, the contents of each liquid trap were poured into a preweighed vial and the solvent was evaporated on a warm hot plate. Upon cooling to room temperature, the vial and extracted finish were weighed together. Calculation of the amount of finish extracted was obtained by the difference between the weight of the empty vial and the weight of the vial and finish. From the extraction profile, 20 minutes was deemed to be a sufficient dynamic extraction time.

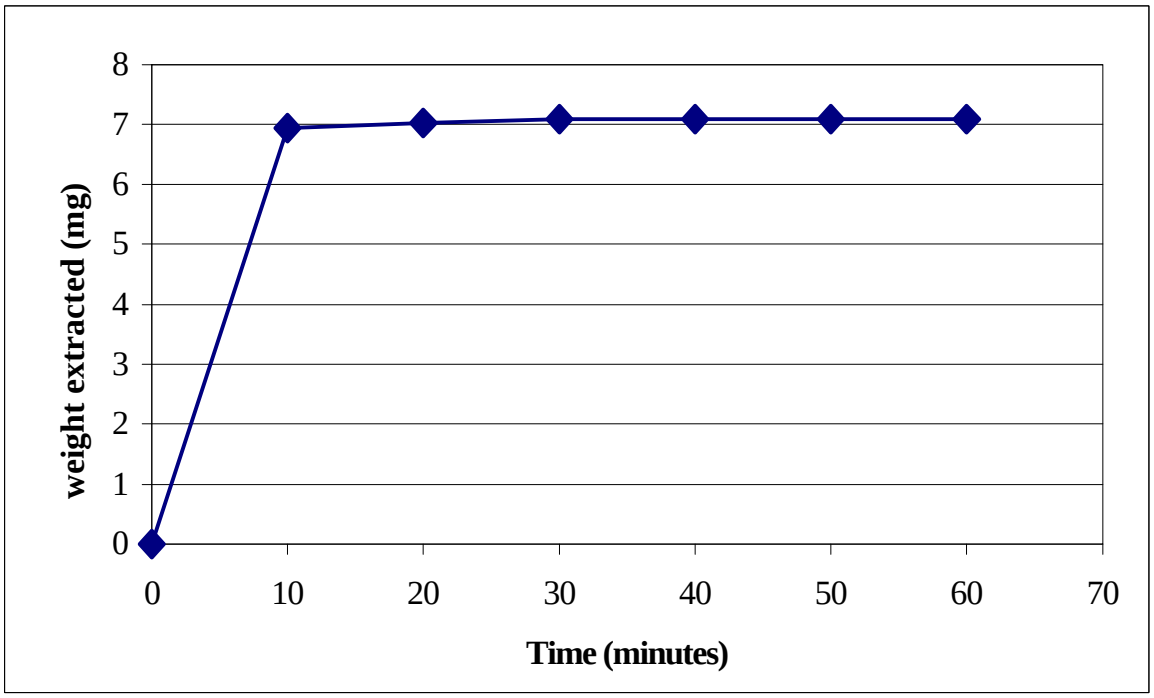

Figure 4. Finish Extraction Profile
Extraction Conditions: control (1) sample, 750 mg fiber, 100% CO_2 at 350 atm, 75°C oven and restrictor, 1.5 mL/min liquid flow rate, 7 mL CH_2Cl_2 liquid trap, gravimetric analysis

Once the appropriate dynamic time was determined, each fiber type was extracted in triplicate and calculation of the %FOY was performed as follows:

$$\%\text{FOY} = \frac{\text{wt of vial after evaporating and cooing - empty vial wt)}}{\text{wt of fiber extracted}} X 100 \quad \text{(Equation 3)}$$

For comparison with the SFE results, conventional solvent extractions of the same fiber samples with chloroform were also performed. In this procedure, 100 mL of chloroform was added to 750 mg of fiber in a 250 mL Erlenmeyer flask. The solution was stirred for 5 minutes at ambient temperature and then the solvent was filtered through Whatman #1 filter paper into another flask. The fibers were rinsed twice with additional 50 mL aliquots of chloroform, which were also added to the flask. The solvent was poured into a pre-weighed, aluminum weighing dish and the chloroform was evaporated on a hot plate. The dish was allowed to cool at ambient conditions and then reweighed. The calculation used for %FOY was performed as in Equation 3.

Results and Discussion

Nylon 6,6 fiber finish was extracted from "control" and "problem" fiber samples by supercritical fluid extraction with 100% CO_2 followed by gravimetric analysis of the dried extracts. The data from the SFE and chloroform extractions are reported in Table IV. Each extraction was performed at least three times on each fiber type. Following extraction there was no change in the appearance of the fibers, although they felt somewhat more coarse when handled. The residue extracted with both methods had a shiny, oily appearance. The %FOY values obtained for the "control" and "problem" fibers with SFE are statistically equivalent to the values obtained via chloroform extraction using F and t tests with 99% confidence levels. The statistics also indicated that the "problem" fibers have a different %FOY as determined by SFE (e.g.=1.2%) but the same %FOY by liquid extraction when compared to the control fibers (e.g. 0.75%). Despite the discrepancy, the extracted finish level is typical for finish on these particular fibers; therefore the difference is probably not significant. Therefore, the residue found

Table III. Finish Extraction Results (n≥3)

SFE conditions: 750 mg fiber, 350 atm, 75°C oven and restrictor, 1.5 mL/min liquid flow rate, 7 mL CH_2Cl_2 liquid trap, gravimetric analysis
Chloroform extraction conditions: 750 mg fiber, 100 mL chloroform, ambient temperature, gravimetric analysis

Fiber Sample	**% FOY (chloroform extraction)**	**% FOY (SFE)**
Control (1)	0.7 (8.4%)	0.7 (5.0%)
Control (2)	0.8 (9.9%)	0.8 (7.4%)
Problem	1.2 (4.7%)	1.0 (7.8%)

( ) indicates relative standard deviation (RSD)

on the processing equipment was not believed to be caused by an excess of total finish present on the problem fibers. For this reason, no further studies were performed on the extracted finish.

A significant result of this introductory study was that the amount of organic solvent used is significantly reduced through the use of SFE. The conventional method required at least 100 mL of chloroform, whereas the SFE method required only 7 mL of methylene chloride for liquid trapping.

Chapter 3

Quantitative Extraction of Nylon 6,6 Oligomers

Introduction

Supercritical fluid extraction with methanol modified CO_2 was employed as an alternative to traditional heptane/methanol liquid extraction for the removal of low molecular weight oligomers from nylon 6,6 fibers. Oligomer quantitation was accomplished via HPLC/UV. The results from SFE and heptane/methanol extraction of all three fiber samples were compared using the statistical methods described in the previous chapter. The main objectives of these experiments were to optimize a SFE method for removing certain oligomeric compounds, and secondly, to determine if the "problem" fiber sample contained an excess of these species compared to the "control" samples.

Experimental

For quantitation of residual monomer on the surface and in the bulk fiber, off-line supercritical fluid extraction with High Performance Liquid Chromatography (HPLC) was used. A standard of a single, raw oligomer was obtained from Paul Seemuth at the Dupont Corporation (Chattanooga, TN) and 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 x 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 HPLC grade and were obtained from Fisher Scientific (Fair Lawn, NJ). The wavelength of UV detection was chosen on the basis of the amide chromophore. The ratio of aqueous to organic portions of the mobile phase was chosen as needed to yield a capacity factor (k') of 2 for the oligomer.

Quantitation of this single oligomer was accomplished by using an external calibration curve that is shown in Figure 5. To generate this curve, a 500 ppm stock 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. A chromatogram of a 100-ppm oligomer standard is shown in Figure 6.

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, Fair Lawn, NJ) contained in 1 mL extraction vessels. The solution was allowed to dry at 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 temp: 75 °C
Dynamic Extraction time: 20 min
Restrictor temp: 75 °C
Solid phase trap: ODS at 75 °C
Flow rate: 1.5 mL/min
Trap desorb temp: 30 °C
Trap rinse: twice with 1.5 mL methanol each

The trap rinses were then analyzed by HPLC. Both rinses 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 shredded and 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. The vessel void volume was filled to approximately 80% with Ottawa sand. Later experiments proved that the shredding step was not necessary, so in the remainder of the experiments the sand filler

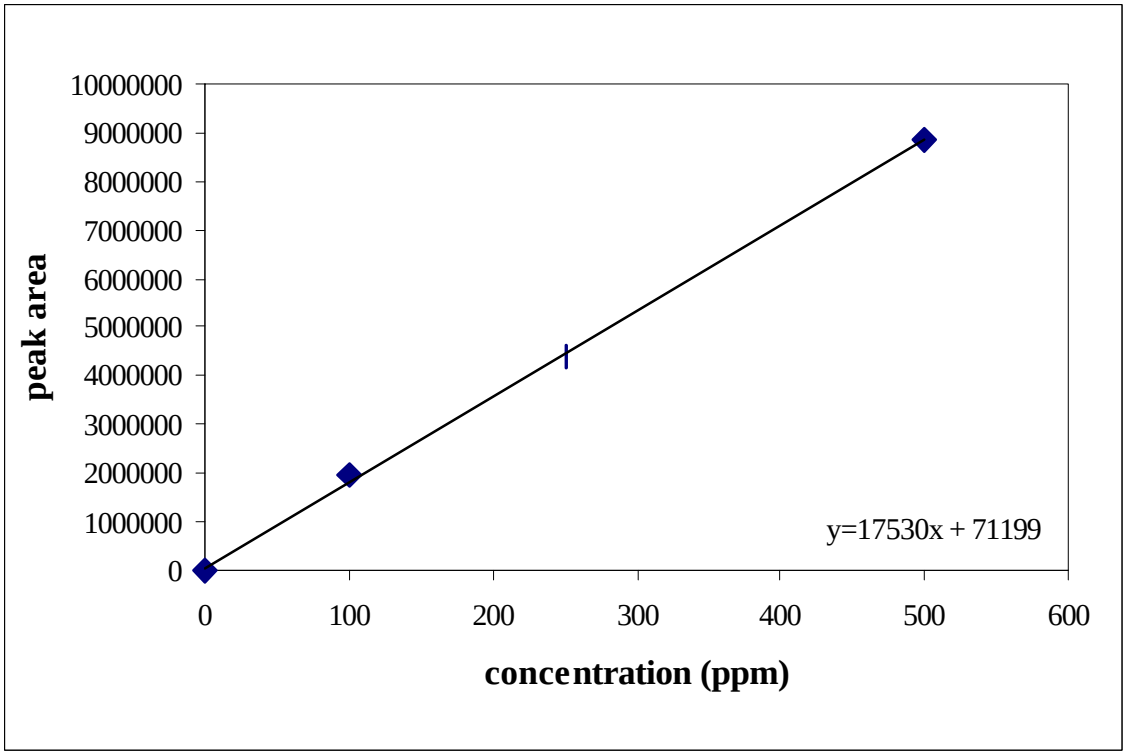

Figure 5. Calibration curve for oligomer quantitation
LC conditions: 250 x 4.6 mm Phenomenex Prodigy ODS (III)column with 5 µm particle size, 70/30 (v/v) H_2O/CH_3OH, 20 µL injection volume, 1 mL/min flow rate, 214 nm UV detection

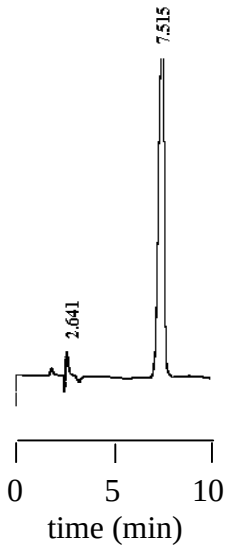

Figure 6. Chromatogram of 100 ppm oligomer standard
LC conditions: 250 x 4.6 mm Phenomenex Prodigy ODS (III) column with 5 μm particle size 70/30 (v/v) H_2O/CH_3OH, 20 μL injection volume, 1 mL/min flow rate, 214 nm UV detection

was omitted since 50 mg of whole fibers occupied the majority of the space inside the vessel.

Conventional liquid-solid extractions with 55/45 (v/v) heptane/methanol as the solvent were performed for comparison to the SFE results. In this procedure, 50 mg of fiber was placed into a 25 mL Erlenmeyer flask and 11 mL and 9 mL of heptane and methanol were added to it, respectively. The mixture was stirred for 1 hour, 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.

Results and Discussion

In the extractions of spiked oligomer from sand, 100% recovery was obtained with both pure and 10% (v/v) methanol modified CO_2. This result was significant for two reasons. First, since spiked oligomer was removed from sand with 100% CO_2, it seemed logical that some oligomer was probably removed from the fibers during the extraction of finish. In order to determine the extent of this, 750 mg fiber portions as received were extracted with the SFE conditions that had been used for fiber finish removal. An octadecyl silica (ODS) solid phase trap instead of a liquid trap was used to allow for direct LC analysis of the extracts from two 1.5 mL methanol trap rinses. The results of these extractions from all three fiber samples are shown in Table V. As predicted, some oligomer was extracted via 100% CO_2. The amount of oligomer removed from the "problem" sample was comparable to the amount removed from the "control (1)" sample. The amount removed from the "control (2)" sample was significantly less. An important fact to note is although some oligomer was removed with the finish extraction conditions, the microgram quantities are probably not large enough to greatly affect the gravimetric quantitation of the finish in the previous chapter.

The result of the spike study was also significant because it indicated that solubility of the oligomer in either pure or methanol modified CO_2 was not a limitation to

Table IV. Oligomer extracted with finish extraction conditions (0.75 g sample, n=3)
Results expressed as μg of oligomer per g of extracted fiber
SFE conditions: 350 atm, 75°C oven and restrictor, 1.5 mL/min liquid flow rate, ODS trap at 30°C, trap rinsed twice with 1.5 mL CH_3OH each

Fiber Sample	**μg/g Oligomer Extracted**
Control (1)	130 (9.7%)
Control (2)	66 (1.1%)
Problem	116 (7.8%)

extraction. Therefore, diffusion of the fluid into the polymer matrix was likely to be the limiting factor for extraction of oligomer from the bulk finish-free fiber. The effects of temperature, pressure, static and dynamic time, spike volume, and percentage methanol modifier were next investigated to determine the optimum extraction parameters for removal of oligomer from finish-free fiber. Results from the optimization study are summarized in Figures 7-11.

As seen in Figure 7, 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. Experiments in which the pressure was varied at constant temperature, as illustrated in Figure 8, indicated that the extraction pressure, and therefore the density, of the fluid is not a critical parameter in the extraction of the oligomer. In other words, recovery was essentially the same at 300, 350, and 400 atm. This reinforces the information obtained from the spike study, in which the oligomer was found to be soluble in both pure and methanol modified CO_2.

Addition of a static step into the extraction conditions did not have any effect on the recovery of oligomer from pre-extracted fiber unless a methanol spike was added (Figures 9 and 10, respectively). As shown in Figure 10, addition of 250 μL of methanol to the vessel prior to a 10 minute static step 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. Addition of modifier prior to the static step may also disrupt various analyte-matrix interactions.

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, as seen in Figure

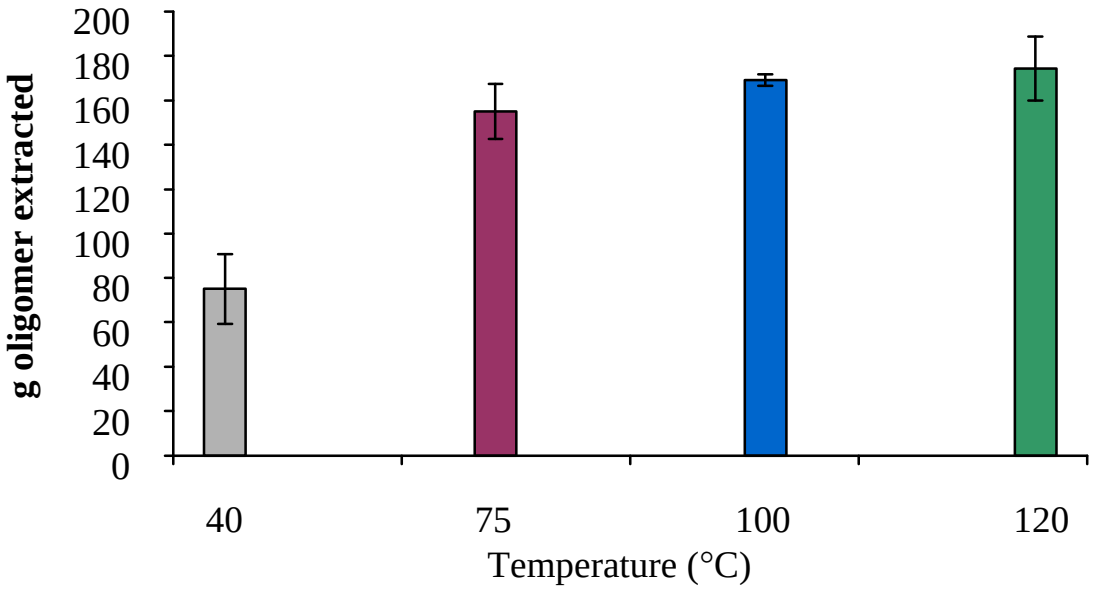

Figure 7. Effect of extraction temperature on oligomer recovery from pre-extracted fiber Other SFE conditions: 90/10 (v/v) CO_2/CH_3OH extraction fluid, 350 atm, 75°C restrictor and ODS trap, 1.5 mL/min liquid flow rate, 30 min dynamic, trap rinsed twice at 30°C with 1.5 mL CH_3OH each, n=3

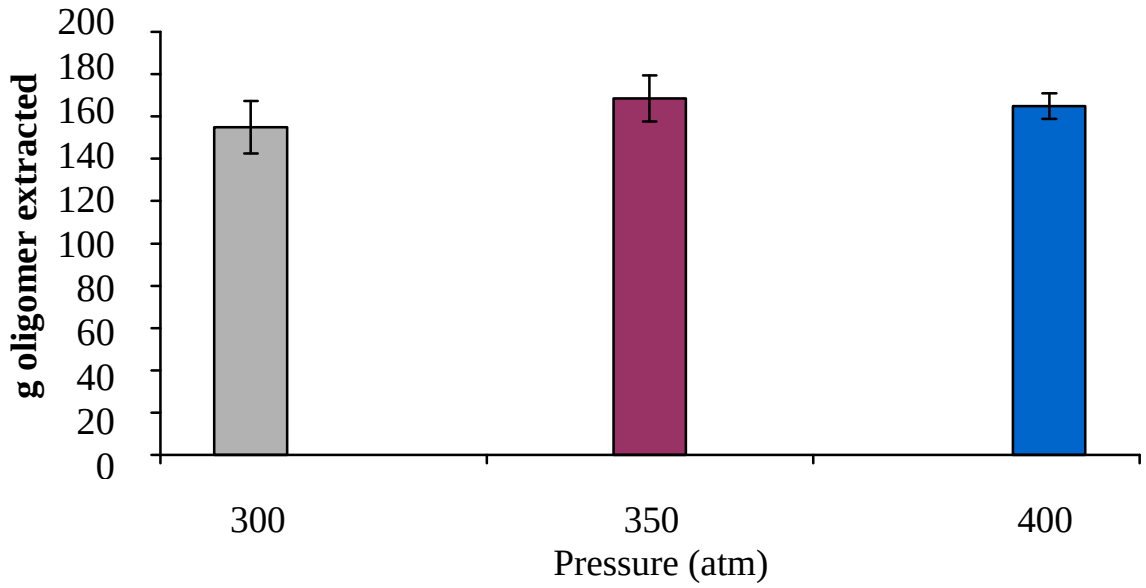

Figure 8. Effect of extraction pressure on oligomer recovery from pre-extracted fiber Other SFE conditions: 90/10 (v/v) CO_2/CH_3OH extraction fluid, 75°C oven, restrictor and ODS trap, 1.5 mL/min liquid flow rate, 30 min dynamic, trap rinsed twice at 30°C with 1.5 mL CH_3OH each, n=3

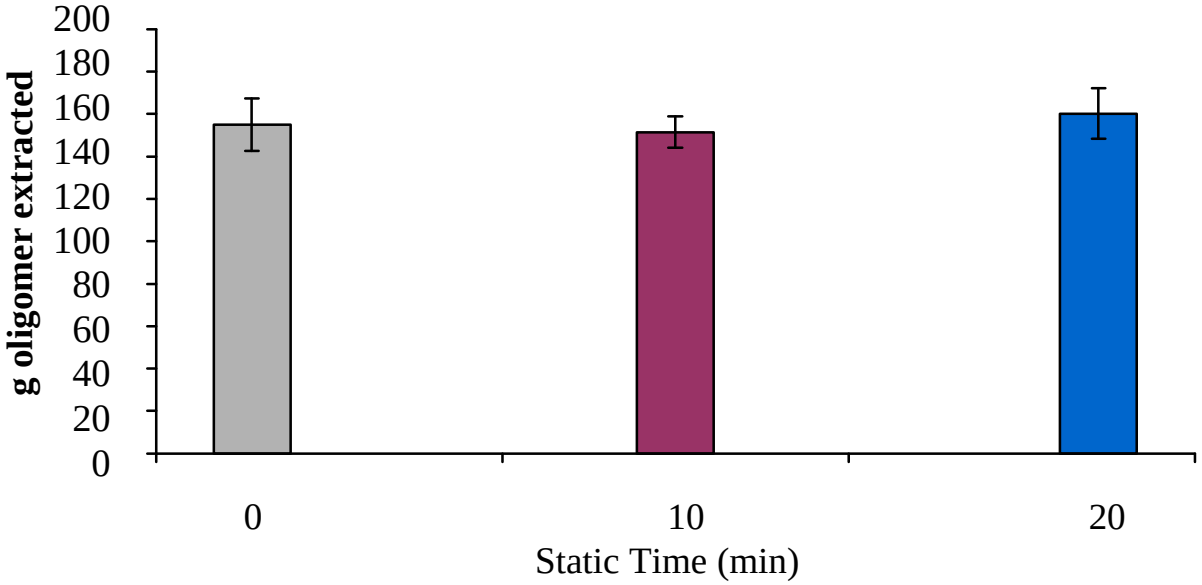

Figure 9. Effect of static time on oligomer recovery from pre-extracted fiber
Other SFE conditions: 90/10 (v/v) CO_2/CH_3OH extraction fluid, , 350 atm, 75°C oven, restrictor and ODS trap, 1.5 mL/min liquid flow rate, 30 min dynamic, trap rinsed twice at 30°C with 1.5 mL CH_3OH each, n=3

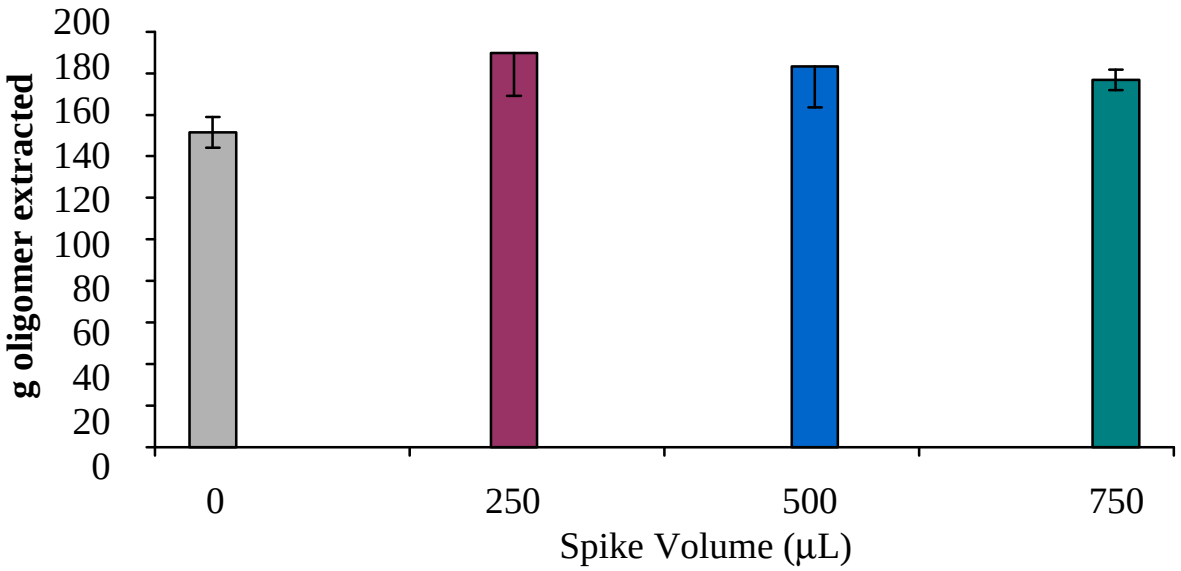

Figure 10. Effect of CH_3OH spike volume on oligomer recovery from pre-extracted fiber
Other SFE conditions: 90/10 (v/v) CO_2/CH_3OH extraction fluid, , 350 atm, 75°C oven, restrictor and ODS trap, 1.5 mL/min liquid flow rate, 30 min dynamic, trap rinsed twice at 30°C with 1.5 mL CH_3OH each, n=3

11. This was expected, since nylon 6,6 possesses polar amide functional groups, it is logical that a polar modifier would aid in extraction of the oligomer. Also, as with the methanol matrix spike, the in-line CO_2/methanol may aid in swelling the amorphous phase, allowing faster diffusion into the polymer.

The extraction conditions chosen for removal of oligomer were therefore:

Pressure: 400 atm	Flow rate: 1.5 mL/min
Temperature: 100°C	Restrictor temp: 75°C
Modifier: 10% MeOH (v/v)	Spike volume: 250 μL
Trap: ODS at 75°C	Trap desorb temp: 30°C
Static time: 10 min	Dynamic time: 15 min
Trap rinse: twice with 1.5 mL MeOH each	

The trap was flushed twice following each extraction and both rinses were analyzed, but the analyte was always contained in the first rinse. The extraction profile obtained for bulk oligomer using the optimized conditions is shown in Figure 12. It was found that the extractable oligomer was removed in the first ten minutes of the dynamic step. These experiments had been performed using 20% methanol modifier, but in subsequent experiments, statistically equivalent results were obtained with 5% methanol modifier, all other conditions remaining the same. Reducing the modifier percentage reduced the amount of organic solvent used for sample preparation even further.

For comparison to the SFE data, conventional solvent extractions using 55/45(v/v) heptane/methanol were also performed as described in the experimental section. The results of the extractions of oligomer from the pre-extracted fiber using both SFE and cold liquid/solid extraction are reported in Table VI. Each value in the Table represents at least n=3 data points. There is no difference between the amount of bulk monomer present in the “control” and “problem” fiber samples as determined by either extraction method. The low RSDs obtained with SFE indicate that using small sample sizes does not cause a reproducibility problem in this technique. Higher precision was obtained with the SFE method, most likely due to the fewer number of steps and therefore the reduction in sample handling compared to solvent extraction.

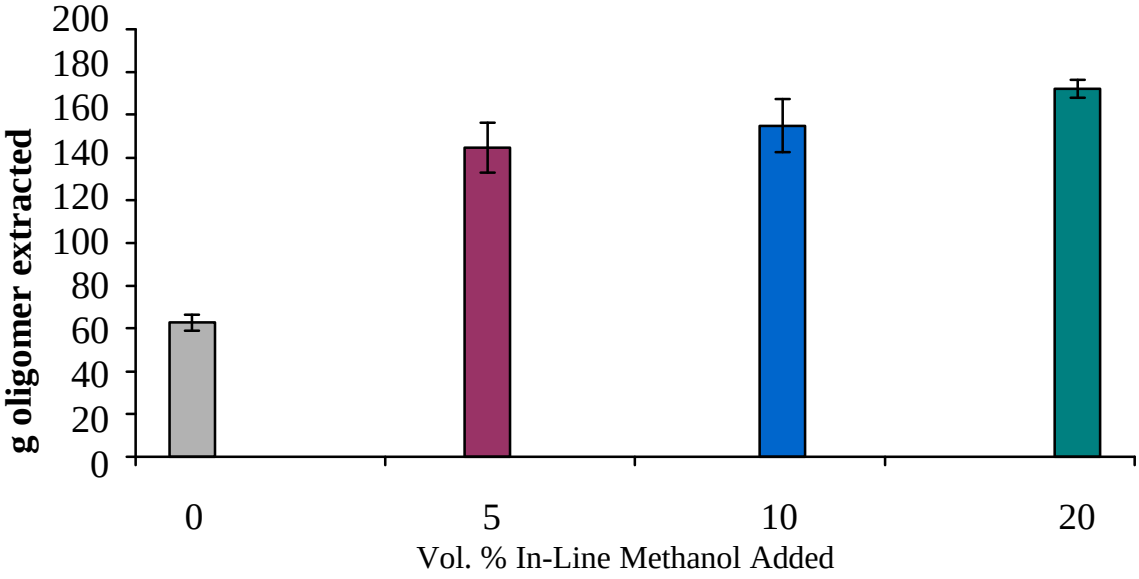

Figure 11. Effect of in-line modifier addition on oligomer recovery from pre-extracted fiber

Other SFE conditions: 350 atm, 75°C oven, restrictor and ODS trap, 1.5 mL/min liquid flow rate, 10 min static time, 30 min dynamic, trap rinsed twice at 30°C with 1.5 mL CH_3OH each, n=3

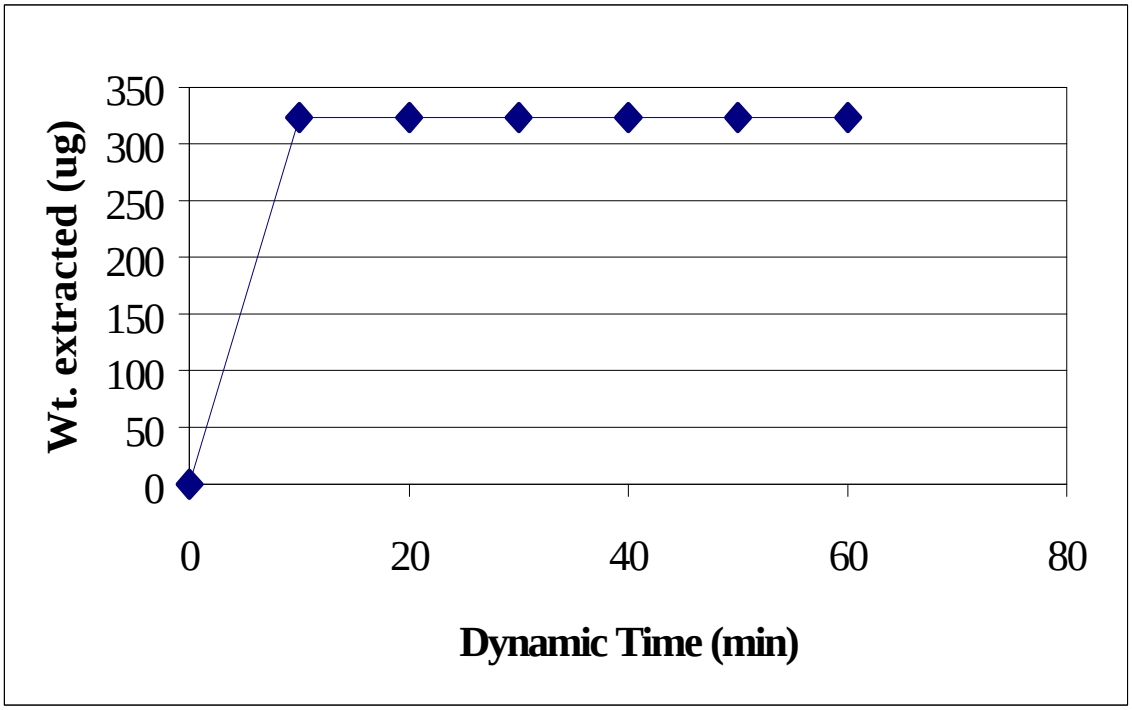

Figure 12. Oligomer SFE profile from pre-extracted fiber
Extraction conditions: 750 mg fiber, 400 atm, 100°C oven, 75°C restrictor and ODS trap, 1.5 mL/min liquid flow rate, 10 min static time, 250µL CH_3OH spike, trap rinsed twice at 30°C with 1.5 mL CH_3OH each

Table V. Oligomer extraction from pre-extracted fiber (n≥3 for each data point)
Results expressed as μg of oligomer per g of extracted fiber
SFE conditions: 50 mg fiber, 80/20 (v/v) CO_2/CH_3OH at 400 atm, 100°C oven, 75°C restrictor and ODS trap, 10 min static step with 0.25 mL CH3OH spike, 15 min dynamic with liquid flow rate of 1.5 mL/min, trap rinsed twice at 30°C with 1.5 mL CH_3OH each, HPLC/UV analysis
Liquid-solid extraction conditions: 50 mg fiber, 20 mL 55/45 (v/v) heptane/methanol, 1 hour extraction, ambient temperature, HPLC/UV analysis

	μg extracted (SFE)	**μg/g extracted (heptane/CH_3OH)**
Control (1) Fibers	6462 (4.5%)	3666 (11.7%)
Control (2) Fibers	6464 (4.4%)	4808 (11.2%)
Problem Fibers	6996 (5.4%)	5390 (12.0%)

( ) indicates relative standard deviation (RSD)

Interestingly, a much larger quantity of oligomer was extracted from the fiber samples with SFE. To confirm this, an extraction profile of the heptane/methanol extraction process was plotted and is shown in Figure 13, with the SFE profile shown again for comparison. It can be seen that after one hour of soaking in the solvent, oligomer continues to be removed from the fibers. This is in sharp contrast to the SFE profile, where the monomer is completely removed after 10 minutes of dynamic CO_2 extraction (20 minutes total extraction time). This could be due to greater diffusion of the CO_2/methanol into the matrix at the higher temperature of the supercritical fluid extraction, as opposed to the lower temperature liquid-solid extraction. When the heptane/methanol extraction was performed at elevated temperature (50°C) the amount of oligomer extracted was equivalent to the SFE results after 20 minutes of extraction.

Since the analysis method had been developed for only a single oligomer and it had been successfully removed with SFE, it seemed logical that other oligomers might be removed as well. It was found that when the LC analysis for monomer was extended for a longer period of time that a large peak eluted at 31.7 minutes when bulk fiber extracts were analyzed (Figure 14). Since there was evidence of significant band broadening of this peak, the organic portion of the mobile phase was increased from 30% to 50% methanol in order to decrease analyte retention time. The UV wavelength of 214 nm chosen for detection was too close to the UV cutoff for methanol to allow a mobile phase gradient. When the samples were analyzed with the new LC mobile phase, the peak shape of the unknown species improved significantly, and additional peaks were observed in the chromatograms, as shown in Figures 15 and 16 (SF and liquid extracts, respectively). It was hypothesized that these peaks were from additional oligomers present in the extracts, but standards for other oligomers were not available for retention time comparison. Mass spectral analysis of these peaks is discussed in the following chapter.

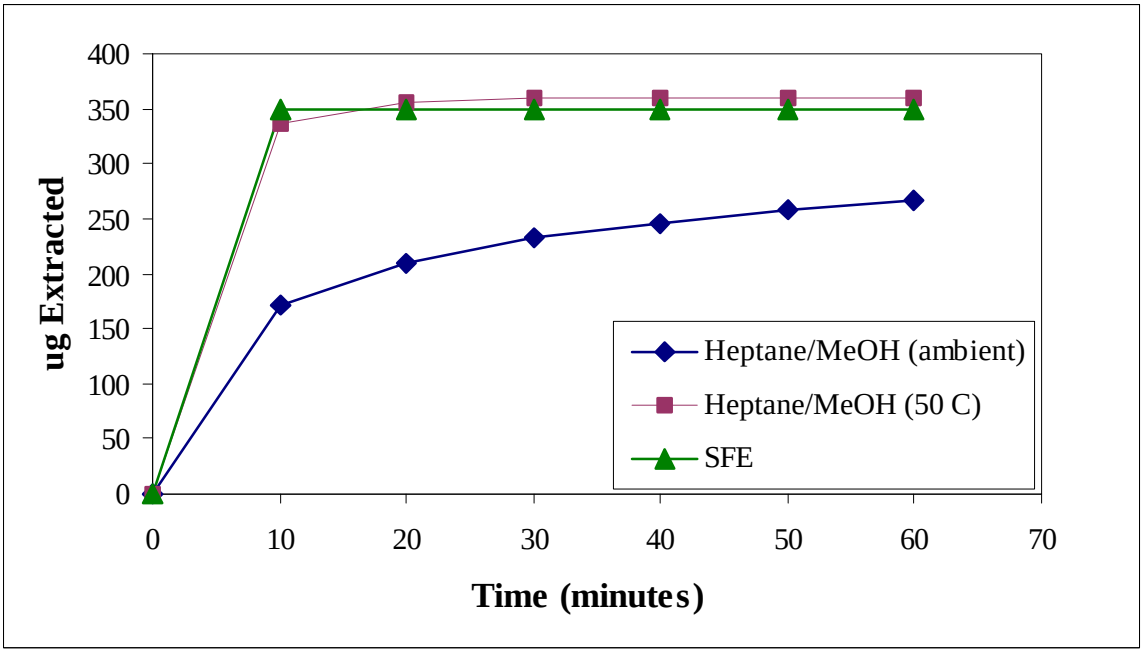

Figure 13: Dynamic SF CO_2 and Heptane/Methanol Extraction Profiles
SFE conditions: 50 mg fiber, 80/20 (v/v) CO_2/CH_3OH at 400 atm, 100°C oven, 75°C restrictor and ODS trap, 10 min static step with 0.25 mL CH3OH spike, liquid flow rate of 1.5 mL/min, trap rinsed twice at 30°C with 1.5 mL CH_3OH each, HPLC/UV analysis
Liquid-solid extraction conditions: 50 mg fiber, 20 mL 55/45 (v/v) heptane/methanol, ambient temp or 50°C, HPLC/UV analysis

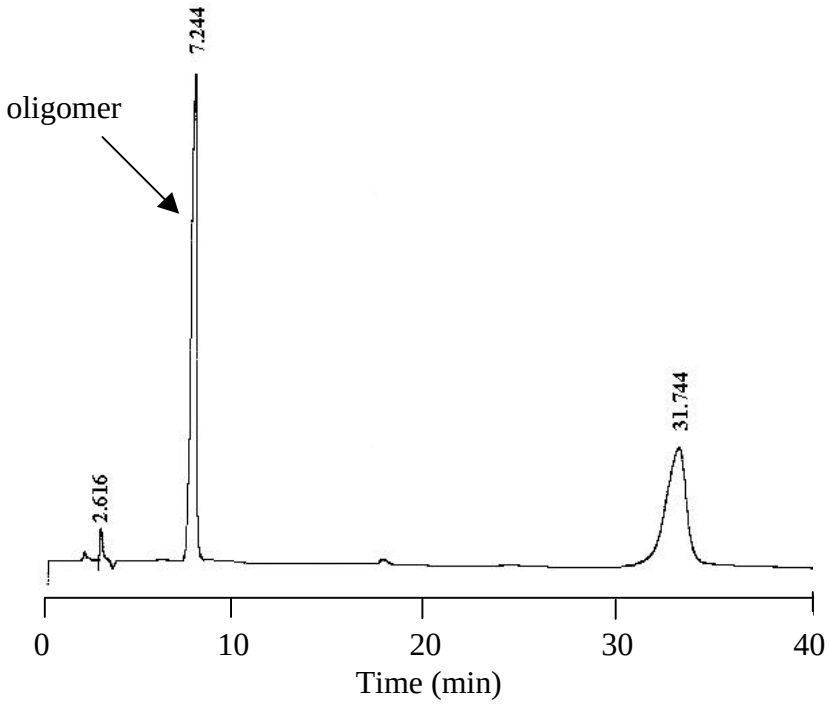

Figure 14: Oligomer chromatogram with extended run time
LC conditions: 250 x 4.6 mm Phenomenex Prodigy ODS (III) column with 5 μm particle size, 70/30 (v/v) H_2O/CH_3OH, 20 μL injection volume, 1 mL/min flow rate, 214 nm UV detection

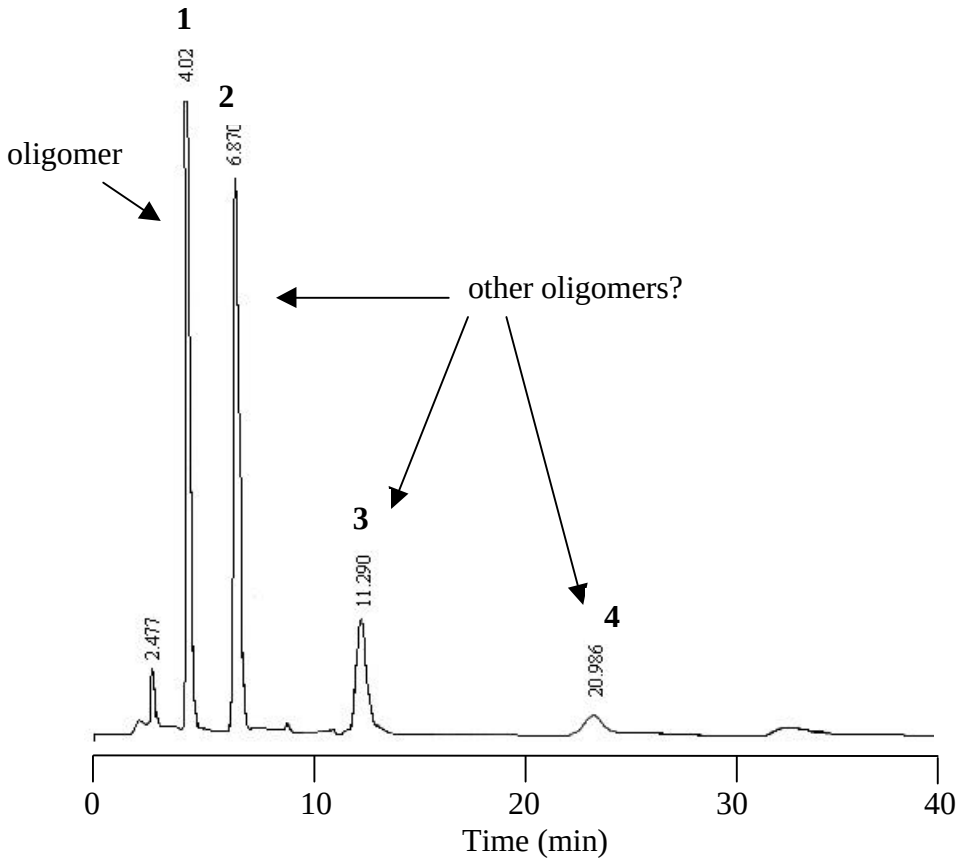

Figure 15: Chromatogram of SF extract of pre-extracted fiber showing other suspected oligomers
LC conditions: 250 x 4.6 mm Phenomenex Prodigy ODS (III) column with 5 µm particle size, 50/50 (v/v) H_2O/CH_3OH, 20 µL injection volume, 1 mL/min flow rate, 214 nm UV detection

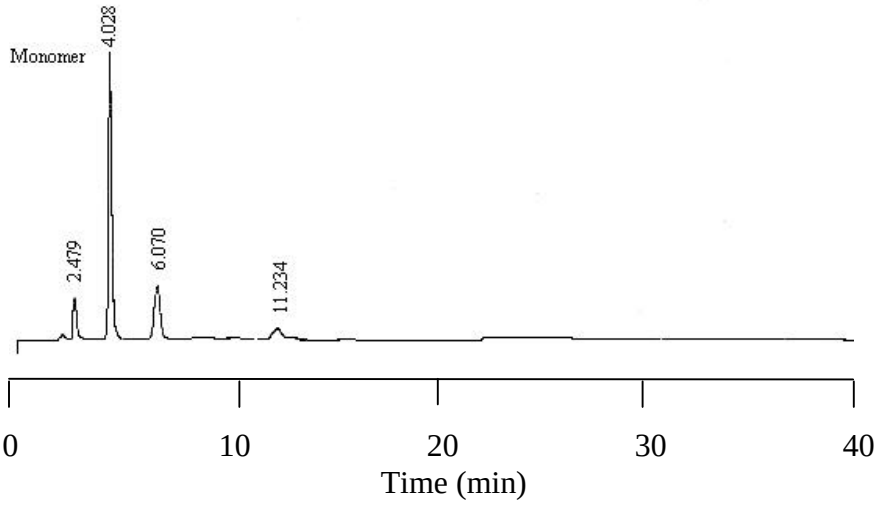

Figure 16: Chromatogram of 55/45 (v/v) heptane/methanol liquid extract of pre-extracted fiber showing other suspected oligomers
LC conditions: 250 x 4.6 mm Phenomenex Prodigy ODS (III) column with 5 μm particle size, 50/50 (v/v) H_2O/CH_3OH, 20 μL injection volume, 1 mL/min flow rate, 214 nm UV detection

In order to determine if the “problem” fiber sample contained an excess of the species contained in these extra peaks as compared to the control sample, the peak areas of the second two peaks from the supercritical fluid extracts were normalized to the area of the known oligomer and shown in Table VII. As seen in the Table, the relative peak areas of the additional peaks from the “problem” fiber extracts are identical to those from the “control” samples. Therefore, the residue found in processing the “problem” sample is not likely from the presence of these additional species.

Conclusions

Supercritical fluid extraction with methanol modified CO_2 was used to remove a single oligomer from nylon 6,6 fibers. Conventional extractions at room temperature and at 50°C with 55/45 (v/v) heptane/methanol were performed for comparison to the SFE data. Higher efficiency as well as higher precision were obtained with the SFE method. The heptane/methanol extraction at room temperature required a one hour extraction time plus time for solvent reduction. The heptane/methanol extraction at elevated temperature may be accomplished in 20 minutes, but the solvent volume must still be diminished. In contrast, the SFE method required 25 min for extraction followed by immediate HPLC analysis, therefore eliminating the solvent reduction step. There is also a decrease in the amount of organic solvent used from approximately 32 mL per sample for total analysis (extraction and HPLC) with the conventional method to about 15 mL with SFE (5% modifier) and HPLC.

Table VI. Normalized areas of additional peaks from fiber extract chromatograms

Fiber Sample	Peak 1	Peak 2	Peak 3
Control (1)	1	0.9	0.3
Control (2)	1	0.9	0.3
Problem	1	0.9	0.3

Chapter 4

Mass Spectrometric Identification of Extracted Nylon 6,6 Oligomers

Introduction

In order to determine the chemical structure of the oligomer standard and extracts, HPLC with on-line Atmospheric Pressure Chemical Ionization Mass Spectrometric (APCI-MS) detection (positive ion mode) was used. A schematic of the APCI interface is shown in Figure 17. In APCI, ions from a corona discharge react with molecules of vaporized mobile phase from the HPLC to produce reagent ions, all at ambient pressure. Since the mobile phase molecules are present in large excess compared to analyte molecules, they are the principal species initially ionized, and in turn charge exchange with analyte molecules. All ions produced pass through a high voltage lens, and are then passed through an extraction cone and skimmer into the MS (29). High sensitivities are often obtained with this technique due to the short mean free path and therefore larger number of collisions between reagent ions and analytes at atmospheric pressure (30).

To confirm the results of the on-line LC/APCI-MS experiments as well as to identify the other species extracted, each peak was fractionated and an off-line Liquid Secondary Ion Mass Spectrometric (LSIMS) system was employed. The ionization technique in LSIMS is analogous to that of Fast Atom Bombardment (FAB) except that an ion beam is used to bombard the solution of analyte instead of an atom beam. It is different from conventional Secondary Ion Mass Spectrometry in that conventional SIMS is employed for the analysis of the surface of solid materials and does not involve the use of a liquid matrix to hold the analyte. In both FAB and LSIMS, momentum transfer from the bombarding atom or ion as well as physical effects from the liquid matrix result in release of secondary ions. Little analyte ion fragmentation occurs, so in many cases analyte molecular weight information may be obtained (30).This technique is useful in that mass spectra may be obtained directly from a liquid sample. The fact that the sample is in liquid form is advantageous in itself in that the surface of the sample droplet is continually renewed from the bulk of the droplet (31).

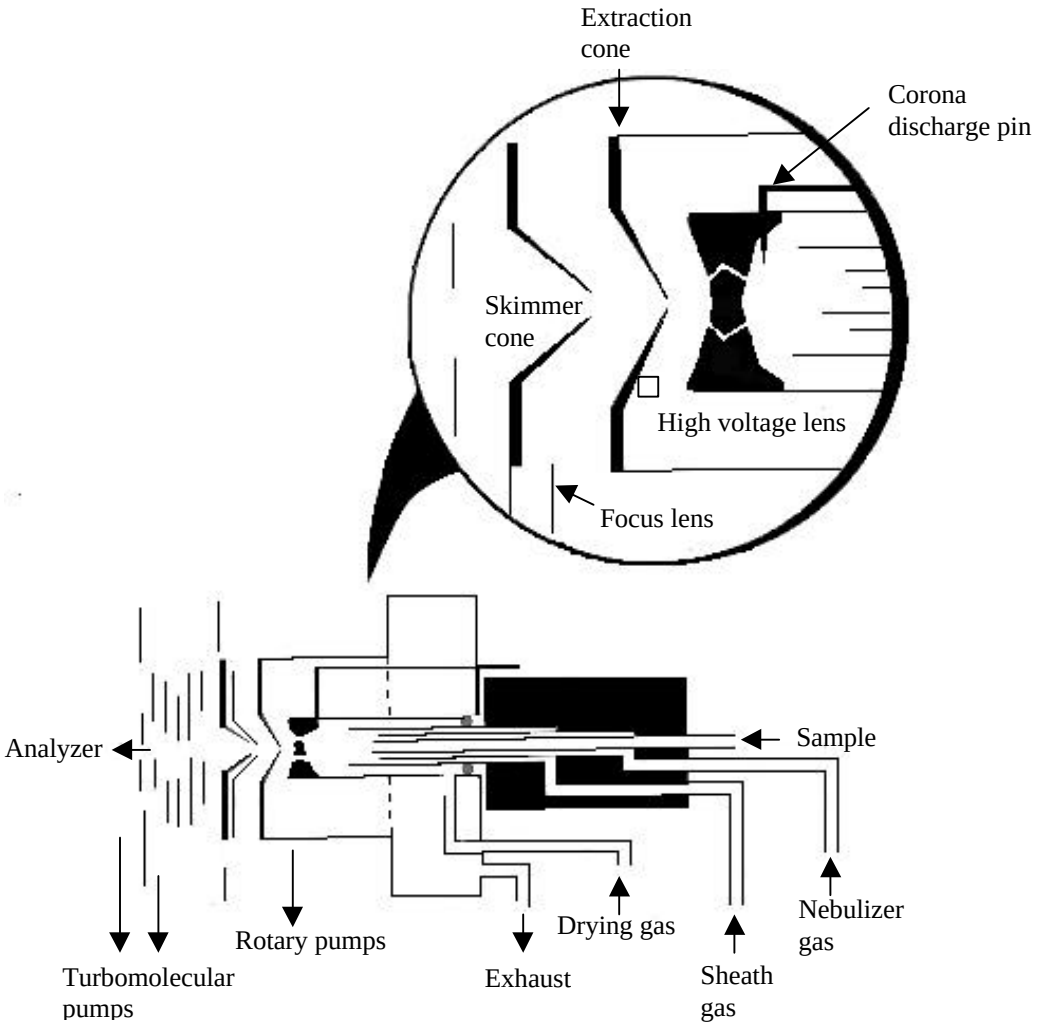

Figure 17. Schematic of APCI interface (taken from ref. 28)

Experimental

A Hewlett Packard series 1050 HPLC and a Micromass Platform/MS with atmospheric pressure chemical ionization were employed in the first portion of the study. The main parameters used were as follows:

LC
column: Prodigy ODS(III) 250x4.6 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 Temp: 400°C
Source Temp: 120°C
Cone Voltage: 30 V
Gain: 3
Mass Range: 100-1000 amu

For the analyses involving direct insertion with LSIMS ionization, a Fisons VG Quattro Mass Spectrometer (Manchester, U.K.) 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 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 sec/scan
Mass range: 100 to 1000 amu

The FB+ ionization mode refers to ionization by FAB or LSIMS in positive ion mode.

Results and Discussion

The chromatogram with UV detection at 214 nm containing the various peaks extracted from the "control" sample via SFE was shown in Figure 15 with the major peaks labeled 1-4. The mass spectra obtained with LC/APCI-MS of peak 1 from the oligomer standard and SF extract (pre-extracted "control" fiber extracted with 10% methanol modified CO_2) are shown in Figures 18 and 19, respectively. The spectra were similar, with a base peak at 227 amu. A list of known oligomers of nylon 6,6, which was obtained from the DuPont Co., is presented in Table VIII. The cyclic monomer has a molecular weight of 226, so it is possible that this peak from both oligomer standard and SF extract from the "control" sample 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.

In order to confirm the results obtained with LC/APCI-MS, HPLC fractions of each peak from a supercritical fluid extract of the "problem" sample were obtained and analyzed by LSIMS. In order to determine the background ions caused by the glycerol matrix, the spectrum of pure glycerol was obtained; Figure 20. Ions of m/z 93, 185, 277, 369, etc. are common in the glycerol spectrum and represent $(glycerol_n)H+$ ions. The spectrum of peak 1 with the glycerol spectrum removed is shown in Figure 21. The base peak appears to occur at 227 amu, which confirms the results obtained by 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 (30). 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 with this technique as well. Figure 22 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 largest ion response in this spectrum, however, occurs at 225 amu, which could indicate that this is a main

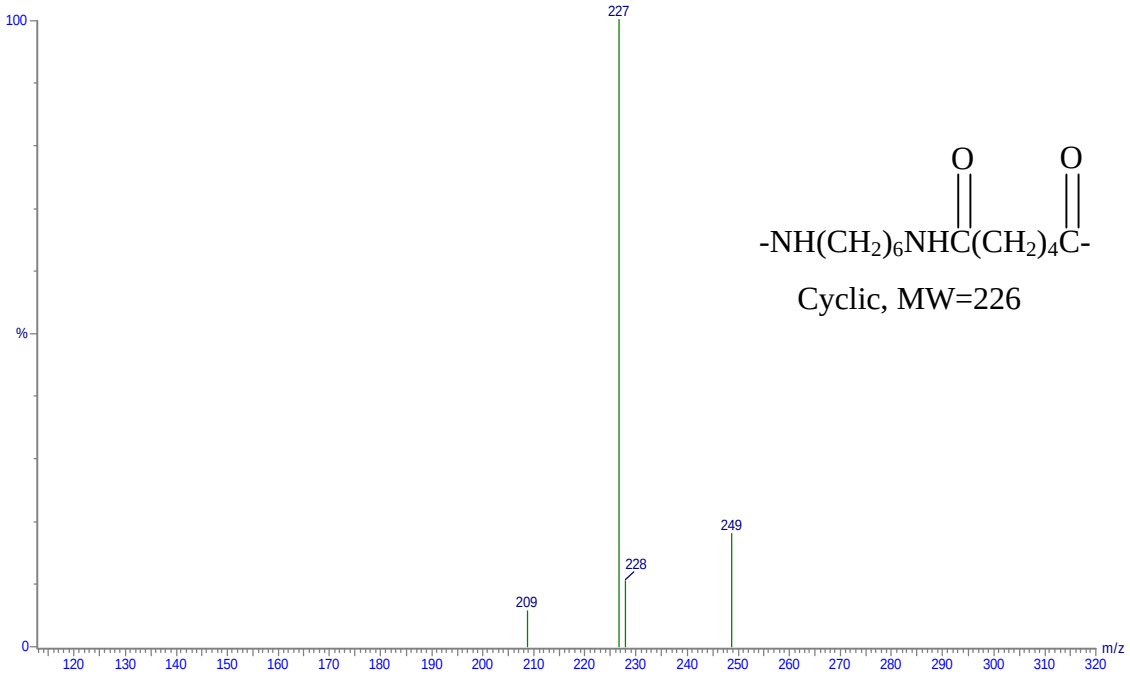

Figure 18. LC/APCI-MS spectrum of 50 ppm oligomer standard
LC conditions: Phenomenex Prodigy ODS (III) 250x4.6 mm column with 5 µm particle size, 70/30 H2O/MeOH isocratic, 10 µL injection volume, 1.5 mL/min flow rate
MS conditions: Ionization: APCI, 400°C probe, 120ºC source, cone voltage: 30 V, gain: 3

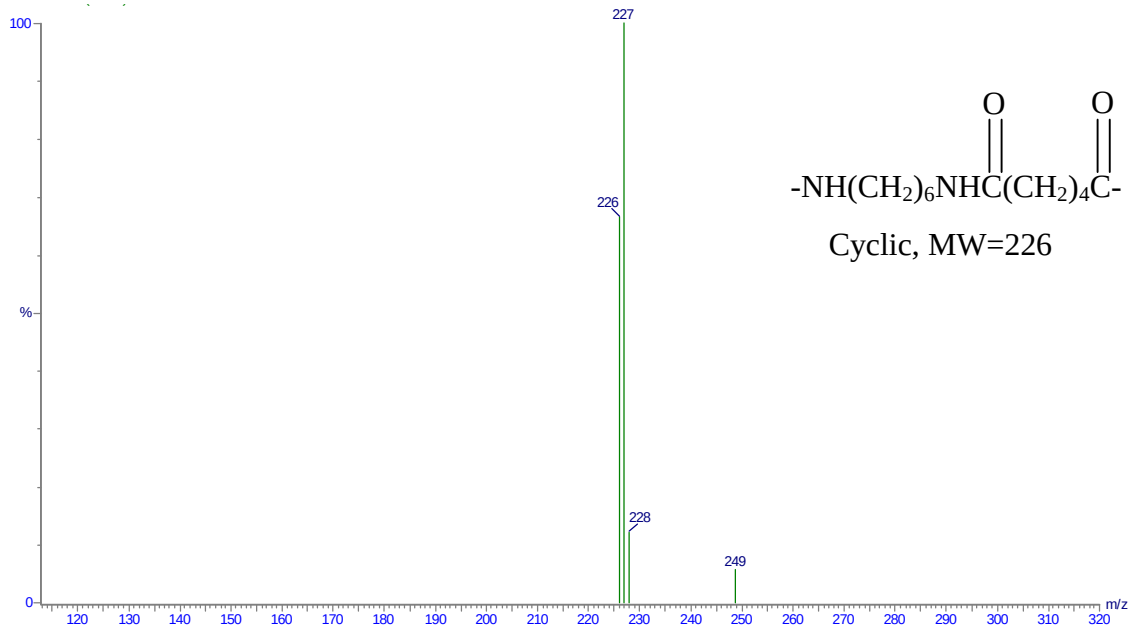

Figure 19. LC/APCI-MS spectrum of oligomer removed from pre-extracted "control 1" fibers with SFE
LC conditions: Phenomenex Prodigy ODS (III) 250x4.6 mm column with 5 µm particle size, 70/30 H2O/MeOH isocratic, 10 µL injection volume, 1.5 mL/min flow rate
MS conditions: Ionization: APCI, 400°C probe, 120ºC source, cone voltage: 30 V, gain: 3

Table VII. Various nylon 6,6 oligomers (obtained from The Dupont Co.)

Oligomer	Molecular Weight
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

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

*C-H = $HO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-$ MW = 129

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

*C = $-\overset{O}{\overset{\|}{C}}-(CH2)4-\overset{O}{\overset{\|}{C}}-$ MW = 112

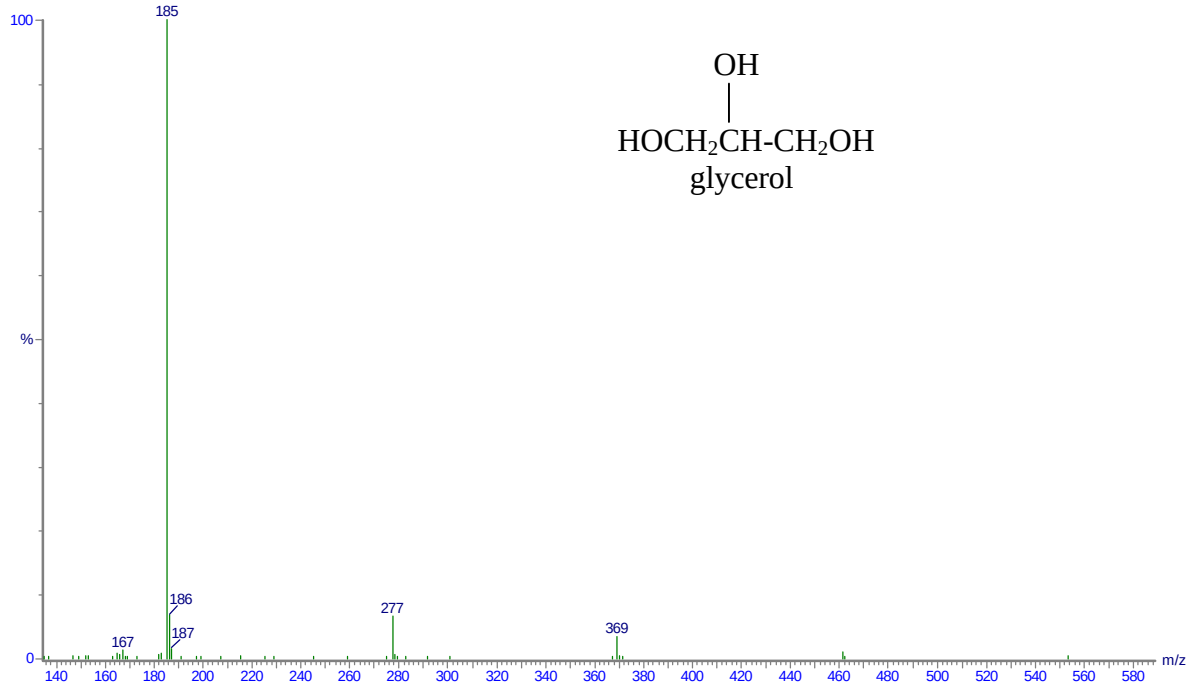

Figure 20. LSIMS spectrum of glycerol

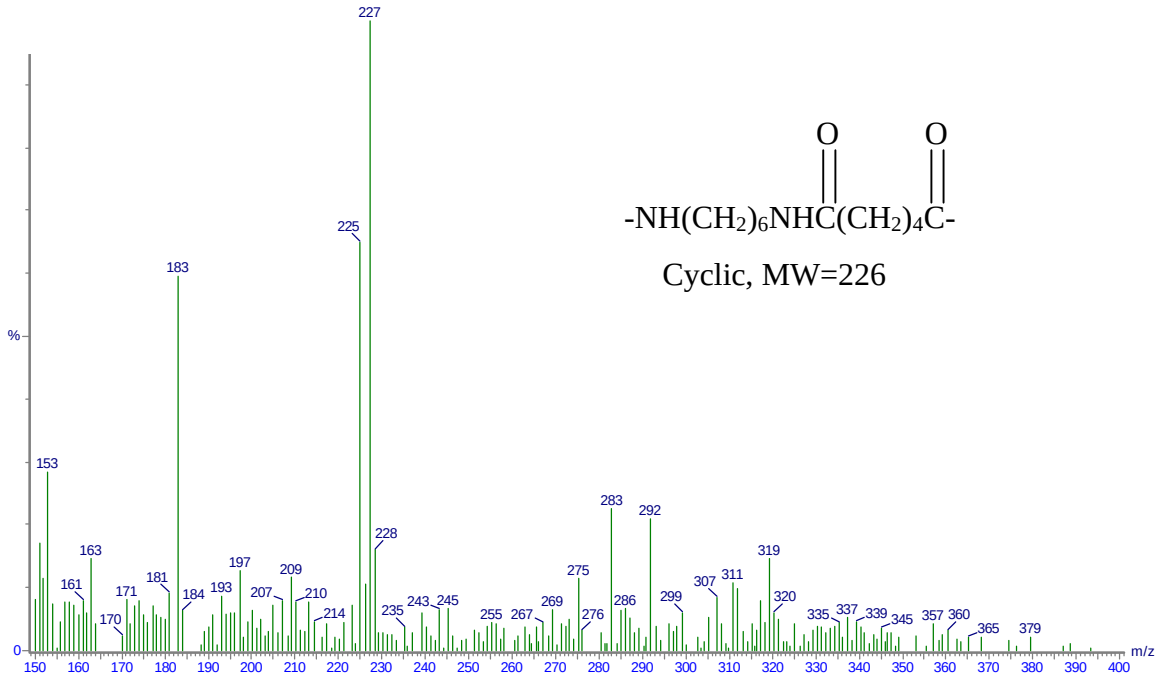

Figure 21. LSIMS spectrum of peak 1 (see Fig. 15) with glycerol spectrum removed

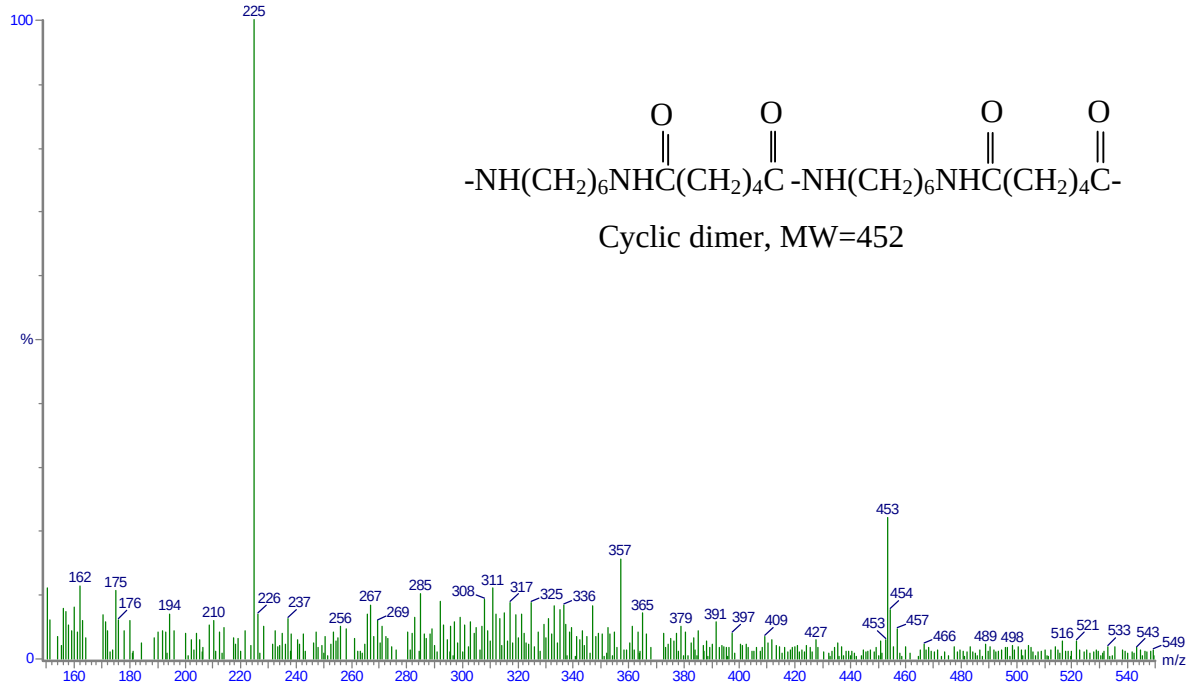

Figure 22. LSIMS spectrum of peak 2 (see Fig. 15) with glycerol spectrum removed

fragment of the dimer. This is a logical conclusion since the 225 ion is also found in the spectrum of peak 1, the cyclic monomer. The identification of peaks 3 and 4 was not as successful using this technique. As seen in Figures 23 and 24, the spectra of both peaks contain a 225 ion which was also found in the spectra of peaks 1 and 2. However, no ion(s) corresponding to any known oligomer of nylon 6,6 was found in either spectrum. Therefore the origin of peaks 3 and 4 in the chromatograms of the fiber extracts is unknown.

Conclusions

In the work described in this thesis, finish as well as low molecular weight monomer and dimer have been removed from Nylon 6,6 fibers with supercritical fluid extraction. Quantitation of finish level as well as weight of monomer in the fiber has been obtained by gravimetric analysis and LC/UV analysis, respectively. It was found that the SFE methods employed offered the advantage of less sample handling and similar reproducibility when compared to conventional liquid/solid extractions. In addition, cyclic monomer and dimer from the SF extracts were identified by LC/APCI-MS and/or direct insertion LSIMS.

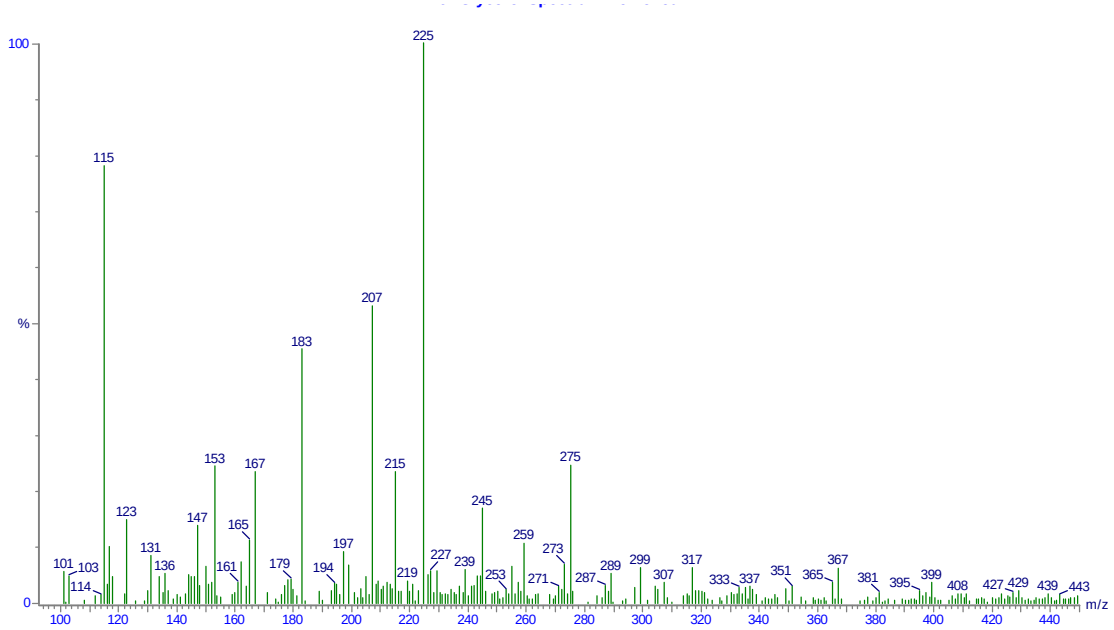

Figure 23. LSIMS spectrum of Peak 3 (see Fig. 15) with glycerol spectrum removed

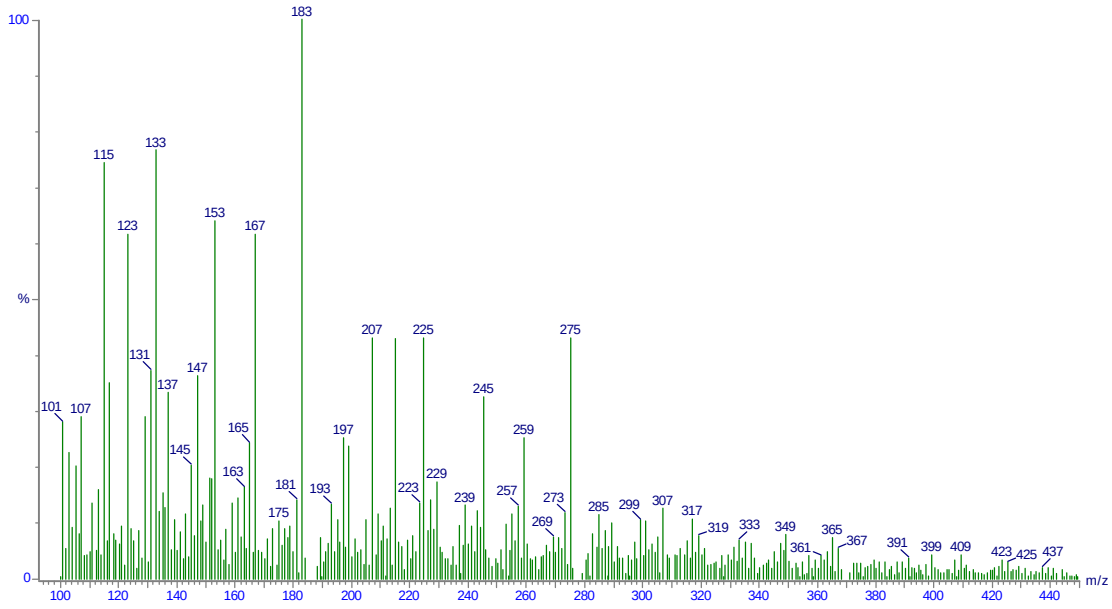

Figure 24. LSIMS spectrum of Peak 4 (see Fig. 15) with glycerol spectrum removed.

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Vita

The author, Shelley Risch Porter, was born on September 2, 1974 to Rev. and Mrs. David Risch of New Eagle, Pennsylvania. After moving to Troutville, Virginia during elementary school, she attended Lord Botetourt High School in Daleville where she developed an interest in the physical sciences. She received her Bachelor of Science degree in Chemistry,cum laude, from Virginia Polytechnic Institute and State University in December of 1995. During her undergraduate years she was privileged to do undergraduate research in the area of adhesion and surface analysis under the advisement of Dr. John Dillard. Following her bachelor's degree she decided to remain at VPI&SU to pursue a Master of Science degree in Chemistry with emphasis in analytical chemistry under the advisement of Dr. Larry Taylor. While at Virginia Tech she was able to participate in several industrial internships, including three semesters spent at Ashland Petroleum Co. in Ashland, KY and two summers working at Monsanto Co. in Pensacola FL.