

## Development of Unique Fibers Using Renewable Resources via Environmentally Friendly Technology

Report Period: June 30, 1994 to July 1, 1995

### Goals

We are developing unique biodegradable specialty fibers from cellulose, chitin and protein raw materials. These are among the most abundant renewable organic compounds on earth but are under utilized, because of processing problems or inferior properties. low strength. The focus of this research is to find production methods which will allow the manufacture of unique fiber products.

### Abstract

Specialty fibers based on biopolymers of cellulose, chitosan and synthetic polypeptides are being developed at Auburn, Georgia Tech and North Carolina State Universities. During the past year we have developed a new NMR technique for determining the degree of deacetylation of chitosan. We have produced highly oriented films of chitosan. Two new forms of chitosan, a graft copolymerized derivative and chitosan/surfactant complex fibers have been developed. Highly concentrated, spinnable anisotropic solutions of cellulose/ $\text{NH}_3/\text{NH}_4\text{SCN}$  as the precursor to high performance cellulosic fibers. We have obtained cellulosic fibers with tenacities as high as 5 grams/denier and modulus greater than 150 grams/denier and chitosan based fibers with tenacities of 3.02 grams/denier and 98 grams/denier modulus. Protein fibers of poly (glycine-valine-glycine-valine-proline) have been produced and cross-linked. This fiber will contract and elongate, reversibly, as the temperature is cycled between  $25^\circ$  and  $40^\circ$  C. Such a fiber could be used as a chemical transducer with a variety of applications in biomedical devices.

### GEORGIA TECH : CONVERSION OF WASTE CHITIN TO NONLINEAR OPTICAL FIBERS

PRINCIPLE INVESTIGATORS: M. B. Polk and R. J. Samuels

#### SUMMARY OF MAJOR ACCOMPLISHMENTS:

We have developed a new NMR technique for determining the degree of deacetylation of chitosan. We have produced highly oriented films of chitosan in the acid form. We have used NMR to confirm the structure of mesogen I. We have also synthesized mesogen II and studied its NMR spectrum. We have also synthesized the homopolymer of mesogen I and determined the three dimensional refractive indices, FTIR spectrum, and X-ray diffraction pattern. We have developed a new NMR technique for the determination of the degree of graft copolymerization of mesogen I onto chitosan.

**GOAL:**

The objective of this study is to establish new applications for chitosan and its derivatives through chemical modification, conversion to fibers and film, structural studies, and property studies; with special emphasis on nonlinear optical behavior.

**INTRODUCTION:**

This project is designed to utilize Chitosan, a derivative of the second most abundant organic material in the world, **Chitin**, for the development and manufacturing of new, natural polymer, liquid crystalline non-linear optical (NLO) fibers. By using **Chitin** as our source we are utilizing, for fiber processing, a waste product from other industries. The project is designed to develop new materials and manufacturing processes, provide trained personnel, and strengthen the nations textile research and educational efforts by uniting diverse experts and resources in a unique collaborative effort,

Organic structures may be attached to polymer chains to obtain films and fibers with good mechanical properties as well as the required optical performance. Liquid crystallinity has been shown to lead to the enhancement of orientation under certain poling conditions. Predicted applications include second harmonic generation, optical modulation, optical switching and memories. In order to achieve these properties, highly ordered systems, incorporating these structures must be fabricated. This project incorporates the following steps to achieve this goal.

- 1) Characterization of the host liquid crystalline polymer chitosan (Figure 1).
- 2) Synthesis and characterization of the NLO mesogens (Figures 2 and 3).
- 3) Graft copolymerization of the mesogen onto chitosan.
- 4) Characterization of the copolymer system.

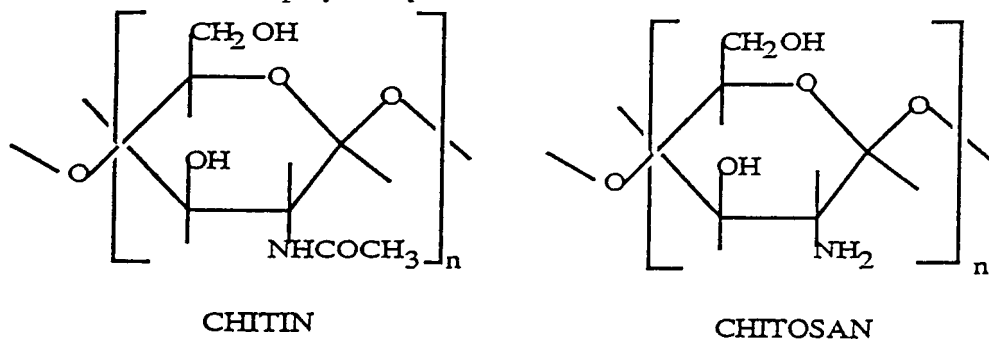


FIGURE 1

**ACCOMPLISHMENTS (THIS YEAR)****1) Characterization of the host liquid crystalline polymer chitosan :**

## a) Determination of Degree of Deacetylation

A new NMR technique for the determination of the degree of deacetylation of the starting Chitosan is under development and is being compared with concurrent titration and infrared measurements. The  $^1\text{H}$  NMR spectrum of chitosan was recorded in a 2%  $\text{CD}_3\text{COOD}$  solution. The solvent signal was suppressed using the PRESAT experiment. Spectra were collected at room temperature,  $60^\circ\text{C}$  and  $80^\circ\text{C}$  respectively. From the NMR spectrum of chitosan, 3 peaks could be assigned unambiguously. The proton that is most downfield shifted (at 4.9 ppm) is the anomeric proton, and the protons that are present most upfield (at 2.05 ppm) are the methyl

protons from the acetylated chitosan (**chitin**). The resonance at 3.1 ppm represents the protons on the carbon 2 of chitosan. The degree of **deacetylation** was found to be about 67% because the integrated intensities of protons on carbon 2 and the methyl resonance are approximately equal. In **chitin** the integrated ratio would be 1:3 and in pure chitosan 1:0. A knowledge of the starting Chitosan degree of deacetylation is essential since it may vary with the source (shrimp, crab), may deform differently, and will effect the limiting copolymer composition.

b) Deformation optimization studies :

In order to optimize the second order nonlinear optical properties of the copolymer the molecular orientation of the host polymer must be at a maximum. It therefore becomes necessary to determine the optimum experimental conditions for achieving very high **orientation**. The effect of deformation path on the structure of as cast **film** was studied by prism wave guide coupling, polarized FTIR, and x-ray **diffraction** techniques. High extensions were achievable from the acetic acid cast films in water. X-ray diffraction indicated a high degree of orientation was achieved. The average refractive index of the stretched as cast film **increases** with time in water during stretching indicating the density (crystallinity) of the film is increasing. Investigation of this system is continuing.

2) Synthesis and characterization of NLO mesogens and Homopolymers:

NLO Mesogen I :

Mesogen I [4-(6-methacryloxyhexyloxy)-4'-nitrobiphenyl] (Figure 2) was synthesised last year (see NTC Annual Report, September, 1994). The <sup>1</sup>H NMR spectrum of the (6-methacryloyl-hexyloxy)-4'-nitrobiphenyl monomer was recorded in CD<sub>5</sub>NO<sub>2</sub> at room temperature. The NMR spectrum confirmed the purity of the monomer. The peaks at 5.4 ppm and 6.2 ppm corresponded to the peaks of the methylene and methine protons of the methacryloyl double bond. In order to study the deformation of the chitosan backbone and the NLO sidechain mesogen simultaneously during deformation of the NLO copolymer it is necessary to first have samples of homopolymer films of each of the components. Films of chitosan have been available for study but not that of the NLO homopolymer. Synthesis of the NLO homopolymer has been achieved and a film produced from nitrobenzene solution. The NMR of the homopolymer was also recorded in CD<sub>5</sub>NO<sub>2</sub> at identical conditions. NMR of the homopolymer indicated an almost complete absence of the alkenyl protons and the appearance of a broad new peak at 1.96 ppm indicating the presence of **alkyl** methylene protons. All coupling information is lost in the homopolymer due to broadening caused by increased viscosity. Wave guide coupling measurements of the film yield an in-plane refractive index value of 1.680, a through the thickness value of 1.684 and an **average** refractive index of 1.681. X-ray diffraction showed random orientation. Thinner **film** preparation for infrared deformation studies are underway. A copolymer film has also been successfully produced as indicated from its infrared spectra.

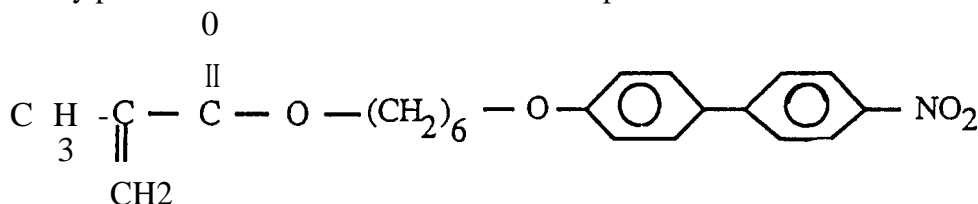


FIGURE 2: MESOGEN I

**NLO Mesogen II :**

Mesogen II [4-(6-methacryloxyhexyloxy)-4'-nitro stilbene] (Figure 3) has been synthesised. In the new monomer the biphenyl group is replaced by a stilbene group, to make the NLO mesogen planar and consequently increase its NLO activity. 4-Hydroxy-4'-nitrostilbene (I) was prepared by the reaction of 4-hydroxybenzaldehyde with 4-nitrophenylacetic acid. The potassium salt of 4-hydroxy-4'-nitrostilbene (II) was obtained by the reaction of I with potassium hydroxide. 4-Hexyloxy-4'-nitro-stilbene (III) was obtained by the reaction of II with 6-bromo-1-hexanol in the presence of 18-crown-6. 4-(6-Methacryloxyhexyloxy)-4'-nitrostilbene (IV) was obtained by the reaction of III with methacryloyl chloride.

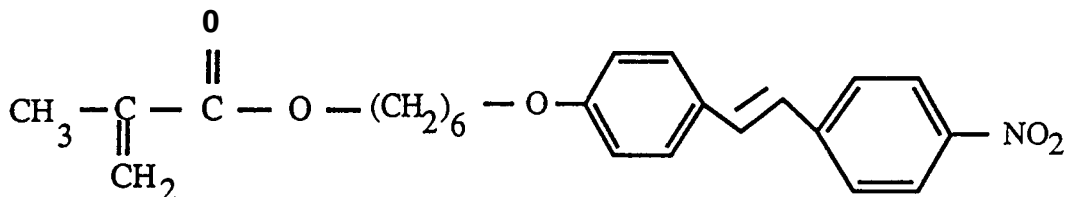


FIGURE 3: MESOGEN II

**3) Characterization of the Chitosan-Mesogen I copolymer system :****Characterization of copolymer composition:**

The NMR spectrum of the graft chitosan was also recorded at identical conditions. Comparison of the integrated intensities of the peaks in the aromatic region to that of proton 1 (the anomeric proton) or 2 gives the grafting ratio. Using the area under proton 2 as the internal standard, the grafting ratio was determined to be approximately 5%.

**EDUCATION****1) Students**

- a) Graduate Students : Vinoid Nair, Wen Ding, Chul Y. Cha and Qing Lian
- b) Undergraduate Students: Bridgette Gomillion

**2) Relevant Publications and Presentations :**

Cha, C., Kim, P. and R.J. Samuels, "Effect of Processing on the Structure of Chitosan Films", SPE ANTEC, 41(2), 1814 (1995).

Kim, P., Cha, C. and Samuels, R.J., "Quantitative Characterization of the Optical Properties of Chitosan Films", MAKROAKRON'94 (35th IUPAC International Symposium on Macromolecules), Akron, Ohio, 7/94.

Cha, C., Kim, P. and R.J. Samuels, "Characterization of the Molecular Properties of Chitosan Films", American Physical Society Meeting, San Jose, California, 3/95.

Cha, C., Kim, P. and R.J. Samuels, "Effect of Processing on the Structure of Chitosan Films", ANTEC'94, Boston, MA, 5/95.

**-- Cellulose --**

Principal investigator: Dr. John A. Cuculo  
Contributing Student: Norman Aminuddin

Ammonia/Ammonium Thiocyanate ( $\text{NH}_3/\text{NH}_4\text{SCN}$ ) is an excellent direct solvent for cellulose. It can form a spinnable anisotropic cellulose solution. In this solution, one observes generally a well defined anisotropic solution of nematic type, composed of individually ordered but randomly positioned domains. Theory has suggested that anisotropic solution can be use to produce a highly oriented fiber. DuPont has confirmed this by its industrial production of the high performance fibers, Kevlar<sup>®</sup> and Nomex<sup>®</sup> and also, for cellulose itself, albeit via a circuitous route. Thus, anisotropic cellulose solutions are considered to be precursors for improved cellulosic fibers.

We have used a highly concentrated, spinnable anisotropic solution of cellulose/ $\text{NH}_3/\text{NH}_4\text{SCN}$  as the precursor to high performance cellulosic fibers. Recently, we have improved the physical properties of the cellulose fibers. Figure 1, presents the cellulose molecular structure for reference. The solutions were spun using the dry jet-wet spinning method into an appropriate coagulant. The extrudate was drawn to achieve a high jet-stretch ratio and thus produced a fine denier of a dense and highly oriented fiber. We have obtained fibers with tenacities as high as 5 grams/denier and modulus greater than 150 grams/denier. We are having difficulty in reproducing consistently these results. One of the main problem is the distortion in the extrudate, commonly known as melt fracture, see figure 2. This is the major source of the uneven fiber denier, resulting inconsistent fiber properties, as reported earlier. The melt fracture, however, occurs at unusually low pressure and reasonably low shear rate. This behavior may be attributed to the rheology of the anisotropic solutions. Although studies have suggested that liquid crystalline solutions are prone to exhibit this behavior, little is known on this matter. Remember that the technology of processing mesophase polymeric solutions is not as mature as that associated with the usual isotropic systems.

Presently, attention is focused on the rheology and characteristic of the cellulose mesophase solutions. The rheology of the anisotropic solutions is being studied using the capillary Instron rheometer. The concentrations of the anisotropic cellulose solutions and molecular weight of the cellulose will be varied. In addition, a potential point of improvement resides in the detailed structure of the anisotropic cellulose solution itself. Attempts will be made to reorganize the overall arrangement of the precursor solution to render it more amenable to coagulating as a dense and highly aligned fibrillar structure.

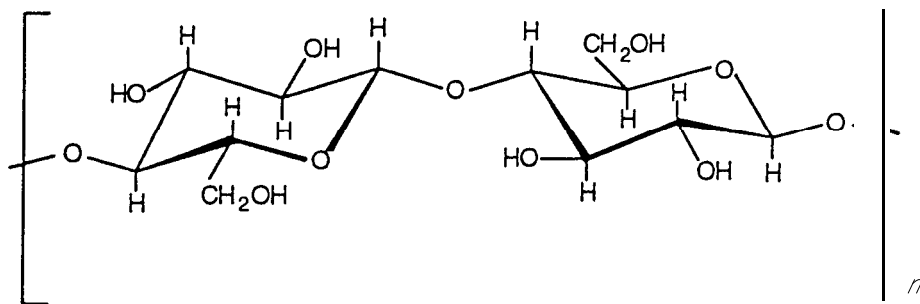


Figure 1. The molecular structure of cellulose.



Figure 2. The extrudate melt fracture from anisotropic cellulose solution viewed under crossed polar microscope.

## Production of Fibers from Synthetic Polypeptides

Investigators: Roy M. Broughton, Jr. David Hall, Ian Hardin (UGA), Dan Urry (UAB)

Protein materials serve a variety of natural function including motility. Proteins which move in response to a stimulus (muscles etc) are actually functioning as transducers. Naturally occurring structural protein materials are reasonable models for synthetic efforts to produce new materials. Materials similar to elastin were produced by one of the investigators (Dan Urry) a number of years ago. Some of the materials produced have been shown to be effective chemical transducers which might be used in a variety of applications including medical devices. These synthetic elastomeric polypeptides change dimensions with changes in environmental conditions, e. g. temperature, ionic strength, pH, etc. One water swollen polymer after being treated with ionizing radiation, exhibits a reversible swelling and shrinking as it is cycled about its critical temperature. The work of this project is to develop a process for making shaped articles, such as fibers, from these materials. The preparation of fibers involves wet spinning followed by crosslinking of the fiber to prevent redispersion of the polymer in water. Small quantities of these polymeric materials have been produced and work on development of crosslinking techniques is underway. Other funded work is directed at large scale polymer production.

The polymeric material which has been produced in the largest quantity (10-20 g) is poly (glycine-valine-glycine-valine-proline) Work prior to the NTC project had produced crosslinked thick films via a molding technique in which the polymer solution (in the mold) was exposed to ionizing radiation. During this project, relatively small fibers have been produced from poly (GVGVP). These have been extruded from water solution into a innocuous coagulation bath and have been irradiated without containment in the mold to produce a fiber having transduction capabilities. The fiber will contract and elongate, reversibly changing its length by some 30 % as the temperature is cycled between 25 ° and 40° C. The mechanism is a folding/hydration process and so the transduction requires a water medium surrounding the fiber. Work funded outside of NTC to produce this polymer via genetically engineered organisms is proceeding well and we expect larger quantities of this polymer for study within a few months. We anticipate an optimized production process for reasonable quantities of the fiber by the end of the project.

Fiber properties for materials produced thus far are shown in Table 1 and Figures 1 and 2. These materials function in a “hydrated gel” state and should not be expected to have the strength of normal textile fibers. Even when dried, the molecules are not well oriented in the fiber direction; so strength is not expected to be in the range of conventional textile fibers. The low strength was still worrisome until a comparison was made with normal muscle fiber. In a rough comparison with normal muscle ( a three-inch diameter biceps for example), a three-inch diameter wool fiber would be able to support a load of about 100,000 pounds, whereas the same sized polyester might support 500,000 pounds. Viewed in this light, we should have perhaps not have expected these fibers to have strength comparable with normal textile fibers.

Contributing Students: Paul Brady, Liming Wang (AU), Chi-Xiang Luan (UAB)

Post Doctoral Associate: Dr. Gang Sun (AU)

**Table1 Strength and Elongation of Polypeptide Fiber**

Fiber Sample	Dry	Swollen
Strength (g/den)	0.18	0.009
Elongation (%)	1.2	250

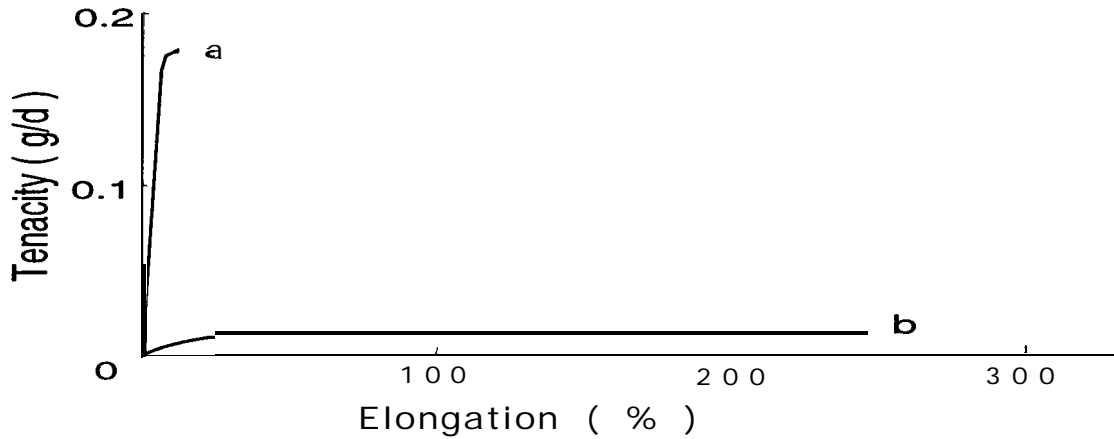


Fig. 1 Stress-Strain Plot of Synthetic polypeptide Fiber  
a-- Dry Fiber b--Swollen Fiber

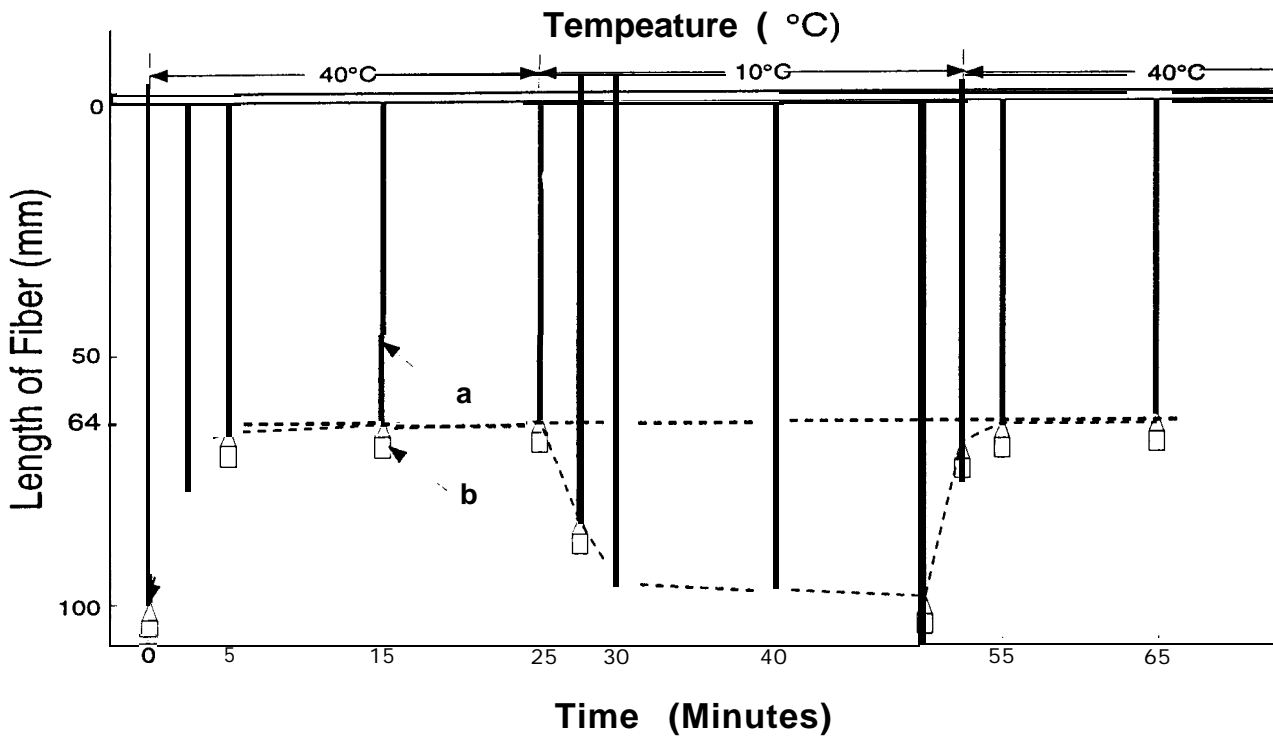


Fig. 2 Reversible Elongation and Contraction Driven by Temperature  
a-- Synthetic Polypeptide Fiber b-- Weight (100mg)

## **Chitin/Chitosan**

**Principal Investigator: Sam Hudson, NCSU**  
**Contributing Students: Monika MacManus**  
**Xiao-Ping Liu**

Hydrophobic chitosan fibers have been extruded and were found to have improved tensile strengths. The presence of hydrophobic domains within the fibers were demonstrated by the absorbance of oleophilic dyes into the fiber. Steps towards a new spinnable derivative of chitosan, based on the Michael reaction of chitosan with vinyl compounds have also begun. Leads from this lab suggest that some vinyl derivatives will lead to highly spinnable, concentrated chitosan solutions with low extensional viscosities.

It has been shown that chitosan fibers can be extruded into a sodium dodecyl sulfate (SDS) coagulation bath. The chitosan polymer flakes are dissolved in acetic acid which protonates the amine groups and makes the spin dope a cationic polyelectrolyte. The coagulation bath consisting of SDS would provide the anionic charge which causes the polymer to precipitate out of solution. A key problem with earlier spinning studies by our group and others has been the coagulation of hydrophilic chitosan in aqueous coagulation baths. This results in a poorly consolidated fiber with inferior tensile properties. By using SDS to form a hydrophobic complex fiber, this problem has been alleviated. To characterize these fibers, a number of techniques were used including tensile testing, FTIR analysis, and dyeing with disperse and solvent dyes. MacManus successfully defended her Master's thesis on May 30, 1995, which chronicles these results.

This research has successfully produced a hydrophobic fiber by extruding cationic chitosan in an anionic surfactant coagulation bath. It was found that a 6% solution of sodium dodecyl sulfate would produce fibers with the best tensile strength. The largest average tenacity was recorded to be 3.02 g/den and a modulus of a modulus 98 grams/denier. After dyeing with two water insoluble dyes, it was determined that hydrophobic regions do exist in the SDS chitosan fibers.

In continuing work with Liu, a reaction product between acrylamide and chitosan via the Michael reaction will be investigated. Earlier work in this lab suggests that this chitosan derivative has a lower extensional viscosity than unmodified chitosan.