

## DOE - Program for Academic and Industrial Research (PAIR) – Final Report

### Real Time Spectroscopic Studies of Structure and Orientation Development in Polymers: Potential Techniques for Intelligent Manufacturing (9/15/99-9/14/02)

Principal Investigator: John F. Rabolt, University of Delaware

Co-Principal Investigator: D. Bruce Chase, DuPont CR&D

#### Personnel

Prof. Kigook Song (Ryoog-Ki University, Korea) – received no salary

Dr. Richard Ikeda (DuPont-Retired) – received no salary

Dr. Sophie Riou Postdoc

Dr. Doug Elmore Postdoc

Simon Frisk Graduate student

Yiaqiang Ding Graduate student

Anand Kalambur Graduate student

Cherish C. Lesko Graduate student

Cheryl Casper Graduate student

Jeannie Stephens Graduate Student

DOE Patent Clearance Granted

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*Date*

Simon Frisk, Cherish Lesko, Sophie Riou (postdoc who worked on poly(ethylene naphthalate) (PEN) for 9 months but left because of medical reasons) and Jeannie Stephens spent approximately 60% of their time working in the DuPont CR&D Lab located 12 miles away from the university. Y. Ding, Cheryl Casper and Anand Kalambur spent less time but their work was primarily centered at the University. They all participated in project meetings, were immersed in the corporate culture, and had access to a diversity of other characterization techniques (e.g., FT-Raman, birefringence, mechanical properties, etc.) which they have used to supplement their current work. They were enrolled in *Analytical Methods in Materials Science* (MSEG 603), a graduate class, where the polarized Raman protocols for measuring orientation in fibers and the “real time” focal plane array IR experiment on a film as it is being stretched were first incorporated.

All students were co-mentored by Dr. Bruce Chase (DuPont) who co-advised their research, attended every bi-weekly group meeting and served on their thesis committees.

#### Accomplishments

During the 3 years of this proposal we have:

- ◆ Developed and perfected a 2-probe “real-time” Raman instrument to measure polarized Raman spectra of fibers on a commercial fiber spinning line. The 2-probe system allows 8 polarized spectra to be obtained without altering the position of the instrument and/or sample.

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- ◆ During the development and optimization phases of this 4 year undertaking we completed static polarized Raman studies of poly(caprolactam) (Nylon 6), poly(ethylene terephthalate) (PET), poly(propylene terephthalate) (PPT) and poly(ethylene naphthalate) (PEN) fibers. Using the polarized data, we have been able to make fundamental vibrational band assignments and obtained an insight into the intermolecular forces responsible for crystallization (in Nylon 6, PPT and PEN) during orientation.
- ◆ We applied this Raman 'polarization protocol' to obtain the first "real-time" Raman spectra of an electrospun fiber as it was spinning.
- ◆ Using the electrostatic forces that occur during the electrospinning process and a judicious choice of processing parameters we were able to create a unique fiber morphology that contains a nanoporous (100 nm) surface structure and, in separate experiments, a "nanoweb" morphology composed of interconnected fibrils as small as 25 nm in diameter.
- ◆ Developed an ultrafast, portable, prototype infrared spectrograph that utilizes a focal plane array detector for "on-line" process monitoring of thin film orientation and crystallization

### ***Research Summary***

The 3-year research program was divided into four parts: the assembly of the instrument, recording spectra of static fibers and filaments, an effort to make the recording of Raman spectra on moving fibers reproducible and the development of a portable, ultrafast IR spectrograph that could be used in "on-line" processing applications. The assembly of the instrument to obtain several polarized Raman spectra simultaneously required the mounting of two sets of collection optics (probe heads) at 90 degrees with respect to one another. A rolling tripod-like arrangement with two long moment arms that hold the probe heads was designed so that they could be brought close to an active spinning line (filaments moving at 155 mph) without interfering with the process. Simultaneously, measurements on static fibers (Nylon 6 (K. Song), poly(ethylene naphthalate) (S. Riou) and PET (C. Lesko)) were carried out in order to estimate the reproducibility expectations (approx. within 5%) for stationary samples. In the process a complete set of vibrational assignments for Nylon 6 were developed for the first time and subsequently published.

Initial reproducibility of the recorded spectra for moving fibers was unacceptable (10-12 %) and a digitally controlled polarization rotator was designed, constructed and adapted to each probe head. This brought the reproducibility down to 5-8% and allowed measurements of PET at various spinning speeds to be made (Figure 1). The question of both precision and accuracy in the determination of  $P_2$  ( $\cos^2\theta$ ) and  $P_4$  ( $\cos^4\theta$ ) orientation functions was then addressed. There was clear evidence for the development of orientation at higher spin speeds and a clear 'break' in the  $P_2$  vs. spin speed curve at 2.5 km/min. This was interpreted as the onset of the crystallization of oriented amorphous chains. It was also found that the values for the Raman tensor for the ring mode in PET at 1610  $\text{cm}^{-1}$  were not constant over the range of spinning speeds that were studied and this may have significant ramifications for previous studies published by others who assumed this was the case. Recently we added the effects of birefringence and local field strengths to the computation, since these were observed to affect the calculation of  $P_2$  and  $P_4$ .

The initial results on PET have been published and the investigation has been extended to poly(propylene terephthalate) (PPT) fibers. The latter were spun (by Simon Frisk) in the labs of Professor Mike Jaffe at Rutgers and were examined to assess the effect of cold drawing on the observed orientation in PPT fibers. It appears that anomalously high values of birefringence develop on cold drawing during the mounting of samples in the sample holder.

Raman spectra of PPT fibers were then obtained at various spinning speeds by Simon Frisk. Polarized Raman spectra of PPT at two spin speeds are shown in Figure 2 (spin speeds of 846 m/min and 4150 m/min). The difference in band intensities (e.g., in the 1300 and 1740  $\text{cm}^{-1}$  regions) is due to the increase in chain orientation with spin speed. P2 and P4 orientation functions can be determined from the full set of polarized Raman spectra and plotted as a function of spin speed as shown in Fig. 3. These plots were created using only the data points that are satisfying our internal redundancy test with a maximum discrepancy of 8%. As seen from Fig. 3 a break appears in the P2 curve at a spin speed of approximately 3.6 km/min and, as in the case of PET mentioned earlier, it is believed that this non-linear increase in orientation coincides with the onset of crystallization in the PPT fibers. The relative degree of crystallinity of fibers at two different spin speeds (846 m/min and 4150 m/min) can be observed in Figure 4 where the 910  $\text{cm}^{-1}$  band characteristic of the crystalline phase is clearly observed to increase at the higher spin speed. The change in the shape of these particular peaks is also a consequence of crystallization. Hence a consistent model for orientation development from the Raman data has emerged. Initially at low spin speeds, amorphous chains are being oriented but no crystallization is occurring. As the spinning speed increases, a highly oriented amorphous phase is observed which then leads to crystallization. The spinning speed at which the onset of crystallization occurs increases from 2.5 km/min (PET) to 3.6 km/min (PPT) as the content of soft segment (-CH<sub>2</sub>-) in the polymer backbone increases.

As we pondered the problem of spinning small amounts of polymer, we began to explore electrospinning polymers from various solvents. Jeannie Stephens, a third year graduate student and Cheryl Casper (a new first year student) set up an electrospinning apparatus and using the "real-time" Raman protocols established for the melt spun fibers, they made "real-time" Raman measurements on submicron fibers as they are being electrospun. As this real time expertise was perfected it was possible to measure, for the first time, orientation functions on electrospun fibers using the orientation protocols developed for melt spun fibers. Jeannie made an interesting observation on the electrospun poly(styrene) (PS) fibers used for the Raman studies. Using a field emission SEM (FE-SEM) to investigate the micro- and nanostructure of these fibers they found the existence of nanopores in fibers electrospun from 30 wt% PS in THF. As shown in Figure 5 under high magnification, a high density (approx. 100 pores/ $\mu\text{m}^2$ ) pattern of 100 nm. pores are observed. This persists down to the lowest concentrations (18 wt%) explored thus far with the observation of a clear presence of both micro- and nanopores at the lower concentrations. Work continued with addition of Cheryl Casper (a new first year student) a comprehensive study of nanopores was undertaken. It was determined that the nanopores appear ONLY on the surface and are a result of evaporative cooling (a "dew" effect) with moisture condensing on the surface as the solvent (THF) quickly evaporates. The droplets leave an "imprint" on the surface before they evaporate. This was verified by reducing the humidity level while electrospinning and showing that the nanopores were not present below 18% relative humidity.

Under a judicious choice of solvent and electrospinning conditions, Jeannie Stephens was also able to produce a unique "nanoweb" morphology with interconnected fibrils of 10-20 nm in diameter. The increased surface-to-volume ratios of these nanowebs make them ideal for applications as air and water filters and as non-resorbable tissue engineering constructs.

Low temperature focal plane array detectors, IR fiber optics and other components of a "no moving parts" focal plane array IR spectrograph were assembled by a new postdoc, Dr. Doug Elmore (Dept. Of Chemistry, Univ. of Georgia) who joined the group in 5/01 to help construct the instrument which was incorporated into feasibility studies of "real-time" studies of orientation in polymer films.

### ***Integration of Research and Education***

From an education perspective, students and postdocs working on this research spend 2 days per week on average at DuPont CR&D labs in Wilmington conducting experiments and working with Dr. Bruce Chase and Dr. Richard Ikeda. The students are exposed and participate in the industrial research culture that provides them with a perspective very much different than that found on campus. Student's participation in the "real world" environment has provided them with additional "workforce ready" skills.

In addition, the polarized 2-probe Raman experiment and the planar array infrared spectrograph was incorporated into MSEG 603 Analytical Methods in Materials Science, a senior undergraduate and beginning graduate (required for M.S. and Ph.D. degrees) course. The students also got some hands on experience obtaining Raman data on oriented fibers and "real time" IR data as a film was rapidly stretched.

### ***Publications***

1. Self-Assembly Through Stepwise Crystallization, Y. Chen, G. L. Baker, Y. Ding, J. F. Rabolt, Journal American Chemical Society (JACS) **121**, 6962 (1999)
2. Polarized Raman Measurements of Uniaxially Oriented Poly( $\epsilon$ -caprolactam), K. Song, J. F. Rabolt, Macromolecules **34**, 1650 (2001)
3. Experimental Determination of the Fiber Orientation Parameters and the Raman Tensor of the 1614  $\text{cm}^{-1}$  Band of Poly(ethyleneterephthalate), C. C. Lesko, J. F. Rabolt, R. Ikeda, D. B. Chase and A. Kennedy, J. Molecular Structure **521**, 127 (2000)
4. "Real-Time" Raman Studies of Electrospun Polymer Fibers, J. Stephens, S. Migelski, S. Frisk, D. B. Chase and J. F. Rabolt, Applied Spectroscopy **54**, 986-989 (2001)
5. Design and Performance of a Planar Array Infrared Spectrograph that Operates in the 3400 to 2000  $\text{cm}^{-1}$  Region, D. Elmore, M. W. Tsao, D. B. Chase and J. F. Rabolt, Applied Spectroscopy **56**, 145 (2002)
6. Studies of Chain Conformation in Triblock Oligomers and Multiblock Copolymers of Ethylene and Ethylene Oxide, Y. Ding, J. F. Rabolt, K. L. Olson, Y.

Chen and G. L. Baker, Macromolecules **35**, 3914 (2002)

7. Arrays of Micro- and Nanopores on Electrospun Polymer Fibers. J. S. Stephens, S. Megelski, D. B. Chase and J. F. Rabolt, Macromolecules **35**, 8456 (2002)
8. Planar Array Infrared Spectroscopic Imaging of Monolayer Films, D. Elmore, C. Leverette, B. Chase, A. Kalambur, Y. Liu and J. F. Rabolt, Langmuir (in press, 1/03)

### ***Patents***

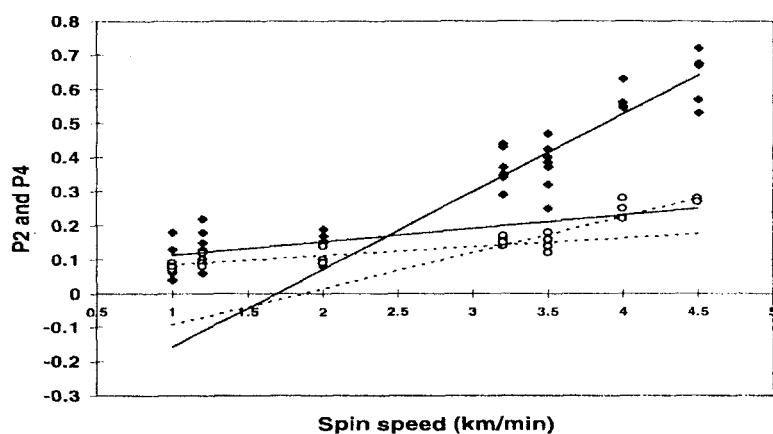
Simultaneous Multi-Beam Planar Array IR (PA-IR) Spectroscopy  
D. Elmore, M. W. Tsao and J. F. Rabolt, Pending  
PCT/US02/08346 filed on 03-19-2002

### ***Impact***

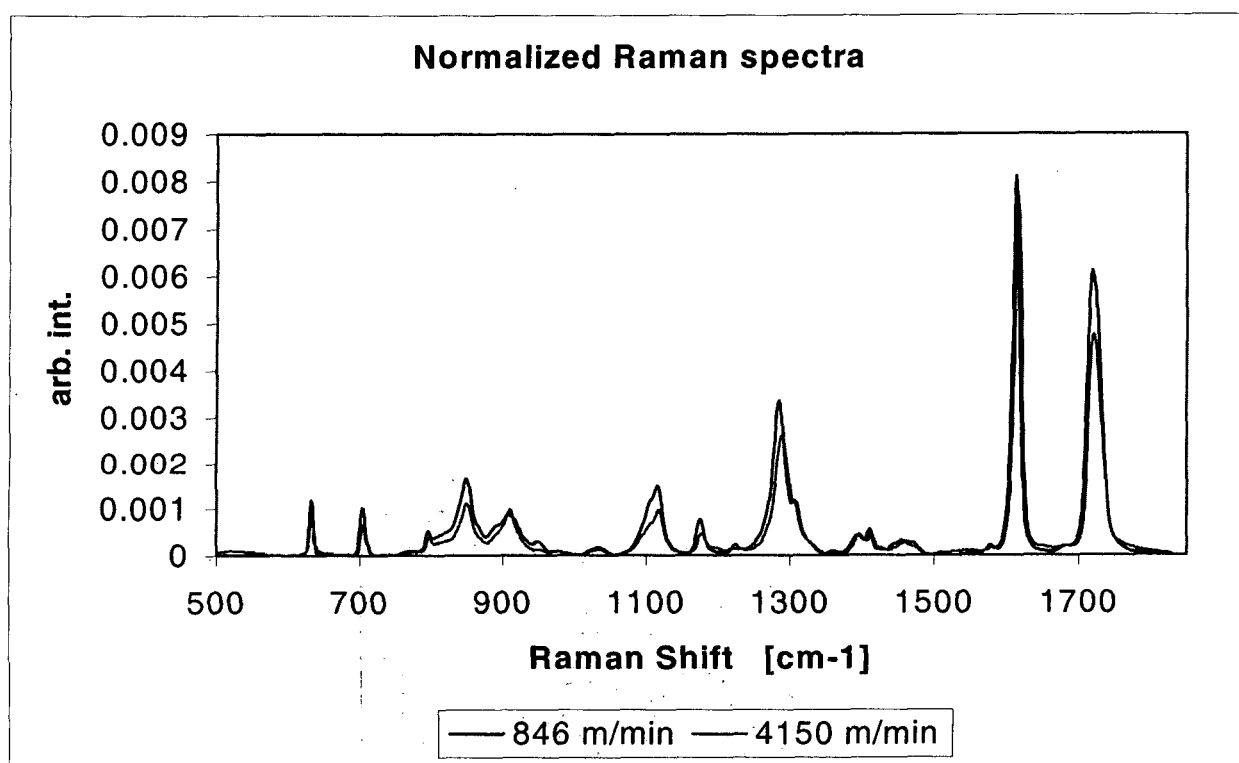
During the 3-year duration of this work, we have obtained new insights into the organization, orientation and crystallization of polymer chains during spinning. By designing a 2-probe Raman system it has been possible to conduct "real-time" Raman measurements of fibers as they are being spun from the melt. Once the protocol was shown to work effectively in determining P2 and P4 orientation functions in melt-spun fibers, the technique was put into use to probe the development of microstructure in electrospun fibers during their formation from electrostatically charged polymer solutions. The development of these generic polarized Raman protocols for determining molecular orientation in fibers can be used in industrial process monitoring to determine the onset of crystallization/orientation and, in general, for quality control.

Throughout these studies, the Co-PIs supervised the research of two postdocs (Sophie Riou and Doug Elmore) and provided motivation and guidance to Simon Frisk, Yiaqiang Ding, Anand Kalambur, Jeannie Stephens, Cherish Lesko and Cheryl Casper so that they would pursue a career in science and engineering. Because of the work that Dr. Doug Elmore did on the development of the portable, ultrafast focal plane array IR spectrograph, he was heavily recruited by industry and joined Cargill in Nashville, Tennessee in March, 2002. Cherish Lesko and Yiaqiang Ding each received an M.S. degree in Materials Science and Engineering in May 2000 while Jeannie and Cheryl have decided to pursue a Ph.D. degree although they both joined this project as M.S. students. Simon Frisk and Anand Kalambur will receive their Ph.D. degrees in August 2003.

The development of Raman instrumentation that uses a 2-probe system to obtain polarized spectra can be used in other research areas for the non-invasive monitoring of changes in structure resulting from temperature/pressure changes, physical aging, degradation, etc. It can also be used to monitor reactions and, based on the results of these investigations, the technique is currently being studied by DuPont for incorporation as a monitor of polymer formation in one of its production plants. On the other hand, the portable, ultrafast planar-array IR spectrograph will have a myriad of uses in *environmental and process monitoring, chemical detection and homeland security*, and as such, must be extended to the important IR "fingerprint" region before it can be used to study kinetics in materials.

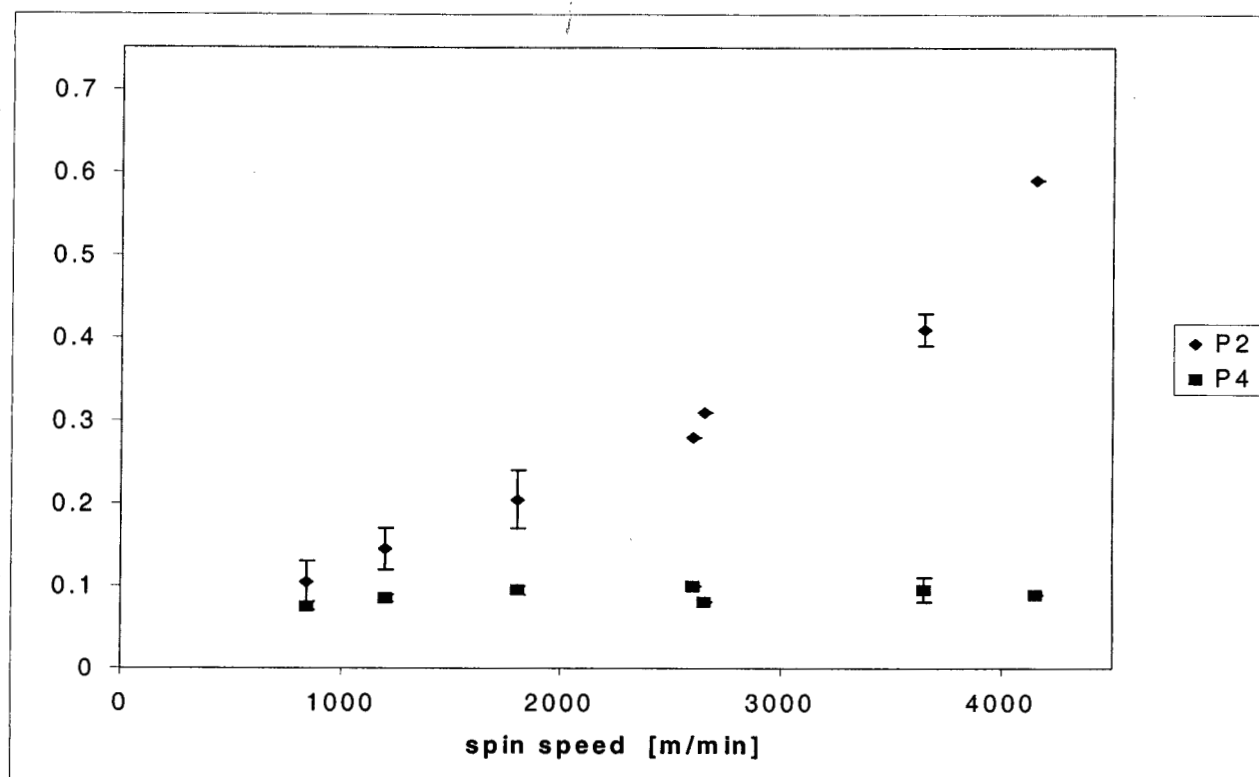


**Figure 1.** Poly(ethyleneterephthalate) (PET) linear regression of  $P_2$  ( $\blacklozenge$ ) and  $P_4$  ( $\circ$ ) values after dividing the experimental data into two sets with spin-speeds of 1.0-2.0 km/min and 3.2-4.5 km/min.

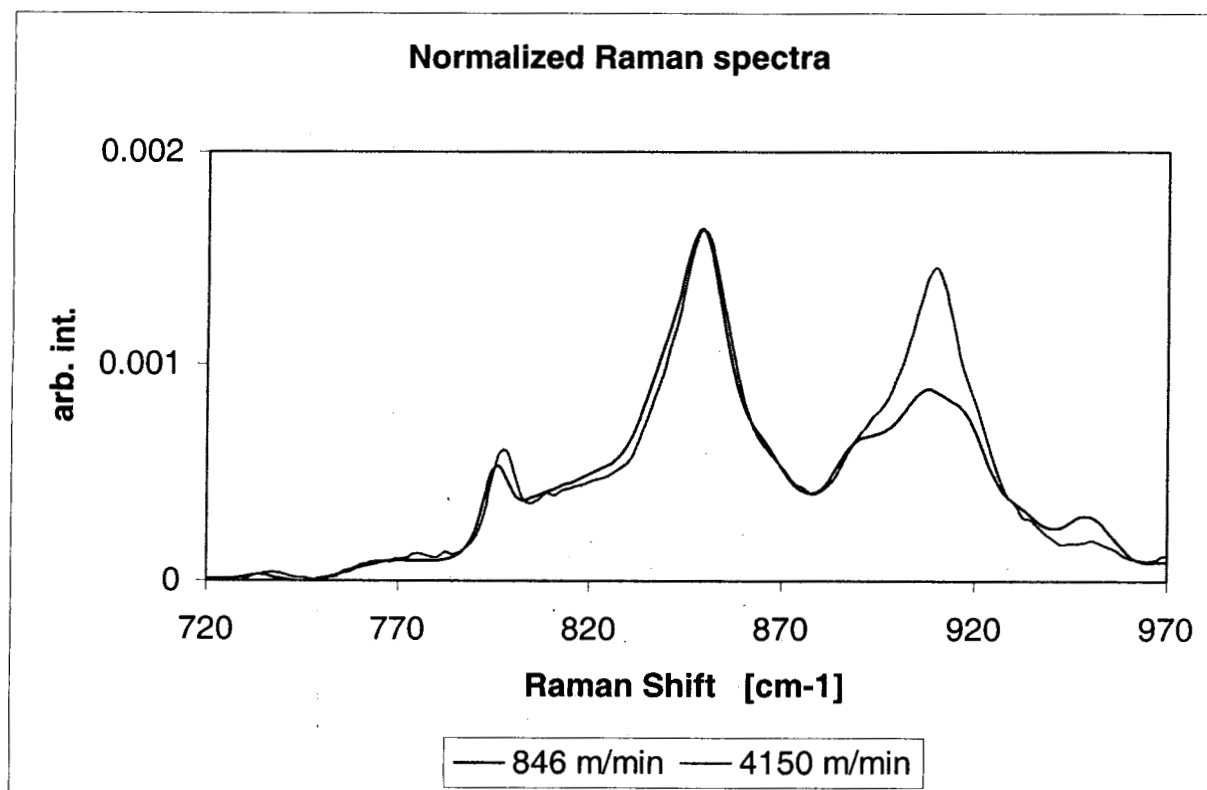


**Figure 2.** Raman spectra of poly(propyleneterephthalate) (PPT) fibers obtained at different spin speeds: 846 and 4150 m/min. Spectra have been normalized using phenyl C-C stretch at  $1616\text{ cm}^{-1}$ .

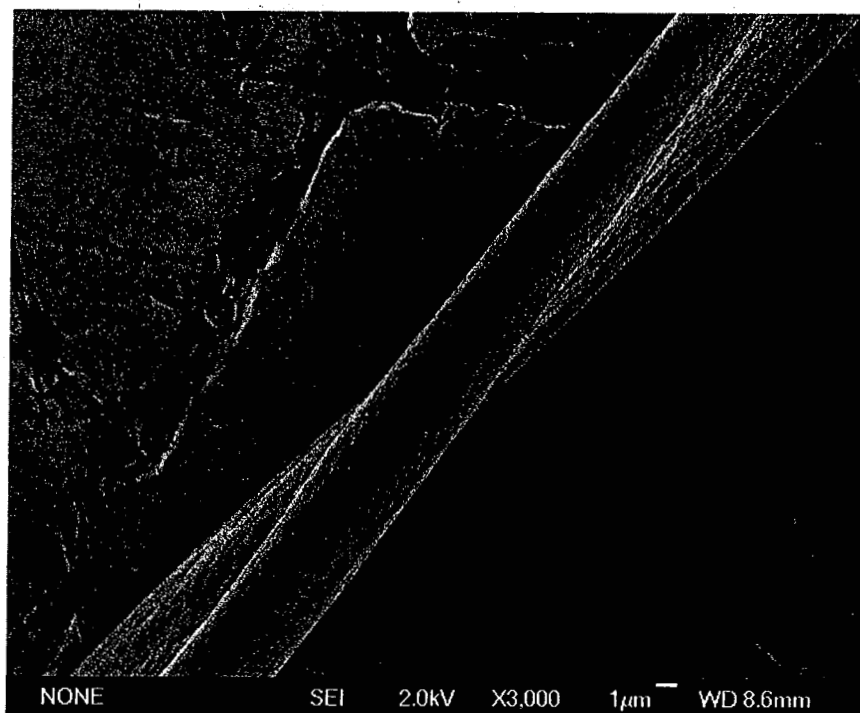




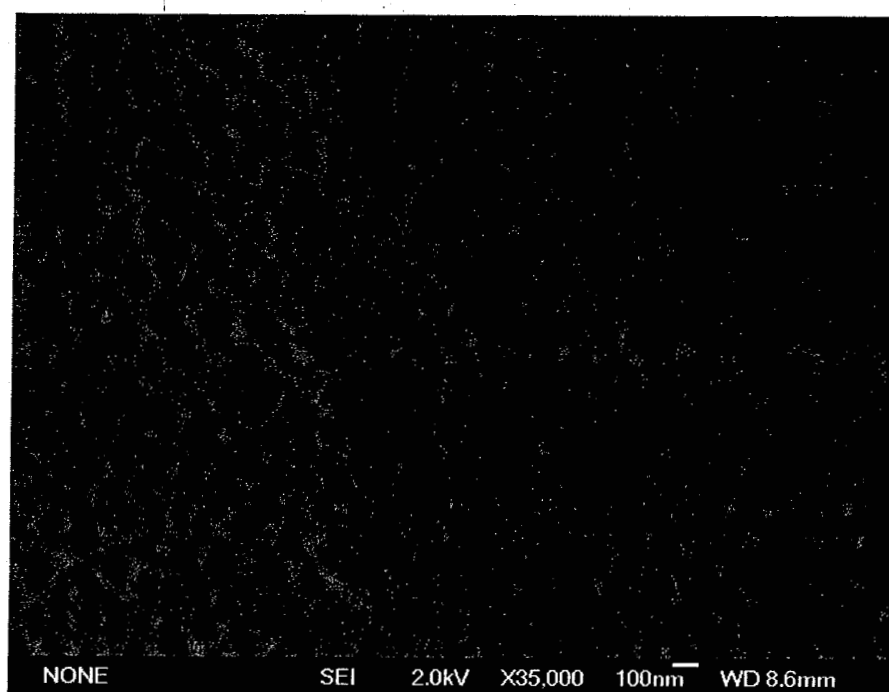
**Figure 3.** PPT Orientation functions P2 and P4 as a function of spin speed.



**Figure 4.** Normalized Raman spectra of PPT in the 900 cm<sup>-1</sup> region as a function of spin speed. The band at 910 cm<sup>-1</sup> is characteristic of the crystalline phase.



A



B.

**Figure 5.** Electron micrograph of PS fibers electrospun from 30 wt. % THF solution.  
 A) uniform diameter electrospun fibers supported on a metallic target (3000X magnification);  
 B) fiber surface texture under 35,000X magnification reveals a high density pattern of nanopores with diameters in the 100 nm range.

The use of polymeric materials is extremely widespread in our lives today. The value of these materials is directly related to various macroscopic properties. High elasticity, toughness, and strength may all be ultimately important to the end user. A large number of analytical tests can be used to measure these macroscopic properties after the material has been processed.

However, it is important to remember that these macroscopic properties ultimately derive from molecular level effects and hence, are already set when processing is complete. Polymers can be extruded into films, spun into fibers, and molded into parts with differing properties, but the understanding of how these properties can be affected by the processing step is unclear. An understanding of the cause and effect relationship between processing, molecular structure and orientation will allow the rational exploration of various processing parameters. The completed research program bridges the gap between fundamental polymer physics and improved manufacturing processes to yield higher value materials at lower cost and with a lower expenditure of energy.