National Textile Center
FY 2004 New Project Proposal

Project No. M04-GT11

Competency: Materials

Nano Scale Polymerization and Fiber Spinning

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Objective:
This proposal is aimed at the design, laboratory production and scale-up with an industrial partner of nylon and polyester nanofibers using the state-of-the-art mesoporous silica nanochannels, and to provide molecular-level understanding of catalysis and flow characteristics within the nanoreactor channels. This is a new revolutionary process with significant advantages. Unlike electrospinning, this new " nano-structured polymerization" process will produce polymers with higher degree of crystallinity, extended chain crystals, superior mechanical properties, and high molecular orientation. A deep insight of the kinetics of nano-structured polymerization and fiber formation must be developed to guide the design of novel nano-polymerization techniques for nanofibers with specific fiber structures. The synergy between experimental and computer aided investigations of this important emerging area will result in a basic understanding of molecular scale processes governing the fundamentals of polymerization, polymer flow, and fiber formation in nanoscale silica channels.
Our main objectives are:
(1) Develop nanoscale polymerization and spinning techniques for polyamides and polyesters and develop techniques to synthesize and harvest nano-polymeric fibers,
(2) Develop atomic scale modeling for fiber extrusion at nano-scales,
(3) Investigate the catalysis process with experiments and simulations to understand the events within silica nano-channels to broaden the applicability of this technique for other polymers.
Our goal is to understand the process and to develop a technique in the laboratory first, and subsequently, once our first year goals are sufficiently met, to work with industrial partners for scale-up and production. We have assembled a team with a unique set of expertise to work on the project and we are confident that we can meet the objectives of this proposal.

Relevance to NTC Mission:
Developments related to synthesizing PE nanofibers using mesoporous silica channels opens up a new dimension in designing and producing fibers with exceptional properties that have not been realized yet. Polyethylene with extended chain crystals has recently been produced using this technique. The race is on for perfecting this technique and extending it for producing nylon and polyester nanofibers. Nylon or polyester with extended chain crystals will provide strength unsurpassed by other materials and could produce the next revolution in the fiber manufacturing area. Such fibers, when produced cheaply, will provide a significant edge for the fiber manufacturers and will result in new applications. Accomplishing this objective at the earliest is our mission in this project. Assembling nanofibers obtained by this technique can be used to produce fibers with varying properties and structures, which will open up a number of new possibilities in the manufacturing of designer fibers. Development of such new promising processes with significant commercial prospects and understanding its fundamentals are well suited with the mission of NTC.

State of the Art:
In 1975, Catani and Kuwata [1] described the radiation-induced urea canal polymerization of 1,3-butadiene. Six urea host molecules per unit cell formed a honeycomb-like canal with a cavity of ca. 5 angstroms along the c axis. Their X-ray diffraction data indicated that there was no periodic heterogeneous structure in a dimension of 100-200 angstroms. Since solution grown single crystals have lamella thicknesses of ca. 94-110 angstroms, they concluded that it was likely that the extended polymer chains in the canals aggregate (coalesce) preferably with one another and crystallize intermolecularly rather than intramolecularly to form lamella. More recently, A. E. Tonelli and associates [2] prepared poly(ε-caprolactone)-

urea inclusion compounds in which the poly(ε-caprolactone) (PEC) chains were confined in the narrow channels (5.5 angstroms) of the urea crystalline host. PEC extracted from the PEC-urea inclusion compound had a DSC melting point of 64^0C compared to a melting point of solution-crystallized PEC of 58^0C. The authors stated that it was reasonable to assume that the extended chain morphology was recovered during the collapse of the urea matrix from the PEC-urea inclusion compound when the urea matrix was extracted with a PEC nonsolvent. Tonelli and his associates are also developing cyclodextrin based self-organization of extended chain molecules [3].

Kageyama et al. [4] has produced linear polyethylene nanofibers of 30 to 50 nanometers in diameter with an ultrahigh molecular weight of 6,200,000 by the polymerization of ethylene with mesoporous silica fiber-supported titanocene with methylalumoxane as a cocatalyst. Since the polymer molecules are produced within the pores of a mesoporous silica (or mesoporous silica fiber), the newly formed polymer chains cannot fold and grow out of the porous structure before they assemble. The mesoporous silica has a honeycomb-like structure with a controllable, but uniform, pore diameter of 15 to 100 A units (similar to the structure shown in Figure 1). It is made up of a hexagonal arrangement of linear capillary channels. The nano-fibers are produced by the polymerization of ethylene with titanocene (Cp_2Ti) and methyl alumoxane (MAO) as a cocatalyst. The polymerization of ethylene in the presence of MAO solid mass results in fibrous PE. Thus, without the post processing-steps, polyethylene macromolecules could be produced and assembled into a fibrous morphology by using regularly arranged nano-scale one-dimensional polymerization reactors. The resulting fibers consist of predominantly extended chain crystals with superior strength and stiffness. By this method high control over the process is achieved for polymers made from simple starting materials.

It was reported that mesoporous catalyst systems containing high concentrations of accessible and structurally well-defined active sites have the potential for controlling olefin polymerization reactions [5,6]. Initial indications of the effect of catalysis on polymer morphology have also been demonstrated. A significant improvement of fiber strength can be achieved by orienting the crystalline regions, and mesoporous silicas have the potential to introduce a new generation of polymerization catalysts, which combine the advantages of tunable, molecular, defined-metallocene catalysts and extended nanoreactors [7]. It was reported that spherical silica gels are already used as supporting materials for the newest Ziegler-Natta catalysts, and new nanoreactors are available for producing fibers with precise structure control.

Approach:

The process essentially involves polymerizing monomers in nano-reactor channels consisting of mesoporous silica, where the chain will be polymerized in the oriented state in the direction of the channel followed by removal of the oriented molecules without disturbing the molecular orientation. Because the polymer molecules are oriented in a specific direction during the polymerization process, the resulting nano-fiber will largely consist of extended chain polymer molecules with higher degree of crystallinity and better mechanical properties than other nano-fibers, such as those produced from electrospinning technique. This new "nano-structured polymerization" technique may be used to prepare extended chain polyolefins, polyamides or polyesters of nanofiber dimensions in the honeycomb-like porous framework of mesoporous silica. The essential steps in this research involves: (1) development of mesoporous silica structure, in some cases infused with acid or base; (2) carry out polymerization reactions in the mesoporous silica channels; (3) removal of polymer chains from nano-channels to harvest the nano-filaments. The initial work will be done with polyolefins, but will quickly move on to other polymers with similar polymerization dynamics. The mechanisms of the ring-opening polymerizations of ε-caprolactone, ε-caprolactam, and 2-pyrroldinone (gamma-butyrolactam) allow us to use this approach to prepare poly(ε-caprolactone), nylon 6, and nylon 4 using anioinic and cationic catalysis. We will focus on synthesizing nano-polyolefin fibers initially because with established methods from the literature we can perfect our understanding of the process and develop methods for harvesting the fibers. The chemistry of the nano-polymerization of nylon 6 and poly(ε-caprolactone) would involve the development of a mesoporous silica infused with acid or base. The mesoporous silica would act as a solid support for bases such as amide ion to produce extended chain nylon 6 by the

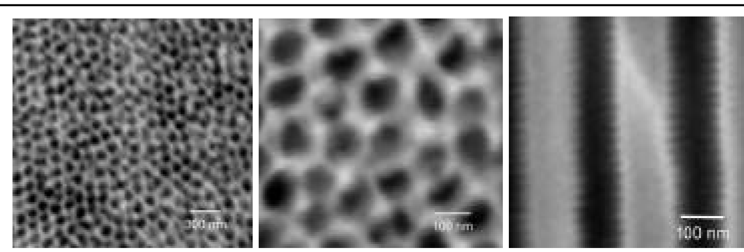

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Figure 1: (a) Pore formation (b) pore widening and (c) longitudinal structure of nano-channels, similar to the structure seen in mesoporous silica (the channel size can be adjusted from 25 to 300 nm).

anionic polymerization of caprolactam. The mesoporous silica can also serve as a solid support for acids such as 12-tungstophosphoric acid to obtain nylon 6 and poly(ε-caprolactone), and would also act as a solid support for methylalumoxane (an anionic catalyst) for the preparation of poly(ε-caprolactone). Methylalumoxane is a cocatalyst for the nano-polymerization of ethylene and therefore would be compatible in the system. Although the reaction restrictions for mesoporous silica prevents the production of PET with current techniques, it is feasible to make a nano-*polylactone* polyester with developments based on current techniques that allow for the incorporation of organosiloxanes containing thiol, amine, or epoxide functionalities into mesoporous silica [8]. Methylalumoxane-supported mesoporous silica is also available. 12-Tungstophosphoric acid has been recently supported on mesoporous silica to produce a very efficient solid acid catalyst for polymerization reactions [9]. The polymerization of caprolactam may be initiated by acids, bases, and water, resulting in nylon 6. Poly(ε-caprolactone) can be obtained by the anionic or cationic catalyzed polymerization of ε-caprolactone. We propose to study the nano-polymerization and nano-spinning of poly(e-caprolactone), nylon 6, and nylon 4 in mesoporous silica nanochannels. By producing polymers with extended chain morphologies, we can increase the thermal stabilities and mechanical properties of the proposed polymer substrates. Major effort will be placed in understanding the process so we can develop a mass scale manufacturing process for these nanofibers in the last stages of our research. A method for separating fibers from mesoporous silica is given in the literature [4]. However, this particular step of nano-structured polymerization process will be studied more carefully to develop faster ways of separating fibers from the mesoporous medium and organizing the resulting nanofibers with the desired microstructure as the development of a faster fiber harvesting technique is important for commercializing this process.

A theoretical/computational effort will be undertaken with the experimental effort to characterize catalyst assisted polymerization and fiber formation. Catalysis has been addressed using first principle *ab-inito* calculations, and nanofiber formation can be addressed using a combination of molecular mechanics/dynamics. The analysis could identify the best structure and dimensions for the mesoporous channels for obtaining the desired fiber structure, conditions for rapid polymerization and fiber formation. Once perfected, this result will aid in the design of the assembly for producing nanofibers. Detailed characterization of the fiber structure and morphology (using advanced FTIR, XRD and EM techniques) together with characterization of the pore structures of the meoporous silicas (using chemisoption methods) will provide experimental insight on the influence of channel dimensions, polymerization conditions and take-up variables on the fiber structure. *Issues to address*: The field is very promising, novel, and rapidly growing; therefore, our efforts will be directed at understanding, developing, and scaling up new processes by building on the existing knowledge. Three issues need to be addressed: (1) an efficient technique of developing meso-porous silica with appropriate structures: Dr. M. Liu (Georgia Tech) has developed and perfected such structures, (2) collection of nanofibers in the desired form: modern techniques used in electrospinning could be modified for our purpose or we could modify the process used in the literature. We will also investigate other new techniques. (3) reduction of time requirements in the process for commercial viability-- this aspect will be addressed once we have a comprehensive understanding of the laboratory process. These issues are important to address, but all them could be easily addressed in order to develop a robust process for producing strong nanofibers through “nano-structured polymerization and spinning”. Scaling up the process and initiation of large-scale production will be achieved in collaboration with industrial partners. We already have one commercial partner to work with during the initial phase and we have support from other companies who will work with us in the scale-up stage.

This Year’s Goal:

In the first year, we will attempt to synthesize poly(ε-caprolactone) by the mesoporous silica-fiber supported methylalumoxane route to obtain "extended chain" polyester formed by the nano- polymerization process. Major effort will be placed in understanding the process. The following specific tasks are envisioned: (1) Design mesoporous silica structures for producing polyolefins and polyesters, (2) Development of a framework to develop a software incorporating catalysis analysis in molecular mechanics to study the polymerization process (3) Preliminary studies to synthesize poly(ε-caprolactone).

Outreach to Industry:

We will work closely with eSpin Corporation as they have significant background on nanofibers. PIs had many discussions with Charge Injection Technologies, and they have expressed significant interest. Discussions are ongoing with other companies.

New Resources Required: No major resources required this year, but in the subsequent years additional resources will be needed.