

National Textile Center

FY 2003 (Year 12) Continuing Project Proposal

Project No.

M01-CL01

Competency: **Materials**

Novel Polymeric Optical Fibers, Fiber Amplifiers, and Lasers

Project Team:

Leader: **John Ballato / Clemson / Optical Properties of Materials; Optical fibers, amplifiers, and lasers**
Email: **john.ballato@ces.clemson.edu** Phone: (864) 656-7881
Members: **Dennis Smith / dwsmith@clemson.edu / fluoropolymer synthesis**
Michael Ellison / ellisom@clemson.edu / polymer melt spinning; polymer physics
Richard Gregory / richar6@clemson.edu / polymer physics

Objective:

This project will fabricate fluoropolymer optical fibers (POFs) that enable the reliable reception, routing, and secured broadcasting of information for use in smart textiles. We will (1) develop synthetic routes to polymers suitable for the manufacture of passive and active POF architectures, (2) draw these materials into low loss plastic optical fibers, (3) coextrude these materials into fibers for comparison to conventionally drawn analogs, and (4) integrate electroluminescent polymer films onto the fibers to serve as detectors and pump sources for the actively-doped, light emitting smart polymer fibers.

Progress Statement:

Parallel research thrusts have been taken to most expediently fulfill our objectives. This includes concurrent efforts in preform fabrication, rare earth doping of bulk polymers (that then will go into the preforms), theoretical computations of optical properties towards compositional optimization, optical source integration onto standard optical fibers (to optimize process for ultimate integration onto the POFs), and die design for spinning bi-component single mode POFs. More specific progress within each topic is now given:

Synthetic Chemistry / Preform Formation Thrust

A variety of difunctional PFCB monomers were prepared and copolymerized with our standard trifunctional monomer. We have continued to focus our process development, optimization and scale-up efforts on the difunctional monomers since the copolymers permit a large tailorability in the resultant optical, thermal, and mechanical material properties of the preforms and, ultimately, the fibers. The precursor bis-phenols are commercially available, allowing direct synthesis of monomers via an efficient two step process. We are happy to report that this versatile NTC supported chemistry has been published in the internationally acclaimed journal, *Adv. Mater.* **2002**, 14(21), 1585.

Recent developments in synthetic procedure have further increased both intermediate product and monomer yields from 30 % to 70 % in some cases. In particular, we have made a fundamental breakthrough on the scale-up process. Originally, both the intermediates and monomer would be isolated by an arduous extraction procedure with large quantities of hexane. We have now developed a superior process whereby the reaction mixture is simply quenched with water, which produces a product precipitate requiring minimal further purification. The solid can be easily isolated on a large scale by simple filtration. This new "Aqueous Process" has greatly reduced organic waste, hazards, and the time for the overall process. These new process adaptations will enable a viable commercial process at a much greater scale and at lower cost. We have continued to prepare high quality trifluorovinyl ether monomers at the 5 L scale with >99.5 % purity. In addition, we have also proven the scalability of the crucial intermediate, $\text{CF}_2=\text{CFO-p-C}_6\text{H}_4\text{-Br}$, at the 22 L scale in collaboration with an industrial partner. Our newly renovated off-campus facility is equipped with a walk-in hood and two 22 L reactors for taking the new NTC funded process to a commercially viable scale. We have optimized the solution copolymerization at the 1 L scale for PFCB monomers in mesitylene solution. The copolymers have been completely characterized (see: *Adv. Mater.*

2002, 14(21), 1585) and copolymer solutions have been supplied to several academic and industrial collaborators as reported in our earlier reports.

Towards the polymer optical fiber amplifiers, rare-earth complexes have been successfully doped into PFCB polymers and their emission detected. We have also prepared a new class of electro-optic monomers and silica-based inorganic-organic hybrid nanocomposites for lower loss and even higher thermal performance. These later cases provide greater optical and electronic functionality, hence value added, to these materials and opens doors to non-optical fiber related smart textile applications. Further, we have recently developed a molding and curing process which gives extremely regular perform prototypes that are as optically clear as glass. The mold and cure process is simple but requires an inert pressure controlled atmosphere during the early stages of polymerization. The process can now be reproduced and several (ca. 10) cylindrical performs have been prepared of varying length and diameter. Figure 1 depicts the photograph of two molded performs from a polymer prepared from the trifunction PFCB monomer.

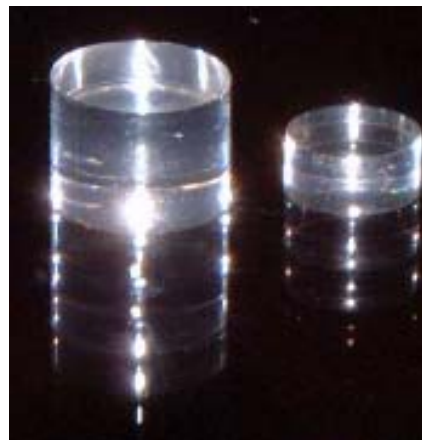


Figure 1. Photograph of PFCB (from monomer 1) molded performs for lenses and POF (10 mm diameter for the perform on the

Co-Extrusion of Optical Fibers

Initial efforts in to extruding bicomponent polymer optical fibers have begun using more traditional spinneret designs. Figure 2 shows the preliminary fibers which were found to possess poor concentricity between core and clad. However, great knowledge was gained in how to coextrude and match viscosities so that new designs, noted below, will move us closer to realization of the goals.

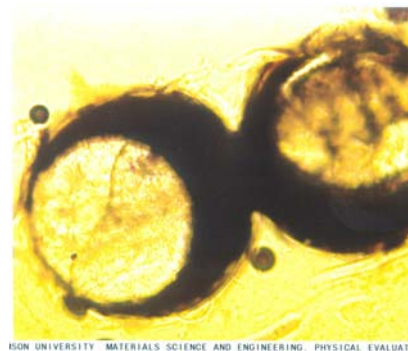


Figure 2. Fibers fabricated by bicomponent extrusion.

Fiber and Amplifier Formation

Clemson's new state-of-the art optical fiber draw tower, funded by DARPA, is now operational and several doped and undoped PMMA preforms have been drawn in to optical fiber for practice prior to starting on the PFCB fluoropolymers.

Next Year's Goals:

It is expected in the few months that we will demonstrate organic microring integration onto active optical fibers. Year 3 will show gain from the microring-pumped active optical fibers. The telecommunication-critical emissions will be characterized in the PFCB polymers. The project also will fabricate PFCB-based step- and graded-index preforms and draw them into optical fiber. Lastly, single mode POFs will be made by co-extrusion and their propagation characteristics (loss, dispersion, spectroscopy for active samples) measured.

Approach:

Synthetic Chemistry / Preform Formation Thrust

Our primary goal for year three will be to leverage the process chemistry success as well as the structure versatility success of this family of optical polymers and mold perform structures suitable for polymer optical fibers. In particular, we will:

- (1) prepare core thermoplastic performs from two homopolymers and varying copolymer compositions there from,
- (2) prepare core/clad and gradient index performs from the same optimized system, and
- (3) develop the draw parameters for successful fiberization.

After we have demonstrated successful fiber draw from these simple and well-established polymers, due to our NTC funded work, we will then investigate the draw of more exotic monomers as well as rare-earth doped systems. As mentioned in earlier reports, we began preparing linear thermoplastic polymers yet suitable performs were not attained at these early stages due to unforeseen discoloration in one case and completely anomalous crystallization

in the other case. We later discovered that precise control of inert atmosphere and pressure improved the process tremendously. In addition we now found that the crystallization can be easily overcome by copolymerization as expected.

Co-Extrusion of Optical Fibers

The requirement of precise control over the uniformity of the sheath/core ratio is being met by a relatively simple modification of the existing BiCo die we employ. Whereas the initial design relied heavily on controlling the flow characteristics of the two polymers by temperature and pressure, we have opted for a new design that will assure a uniform flow over a much broader range of fluid characteristics (Figures 1a and 1b). The flow through this spinneret design will result in a uniform sheath/core geometry. The spinneret is currently being constructed and will be in place by the end of November.

Fiber and Amplifier Formation and Integrated Sourcing

We will reduce to practice the formation of micro-ring all organic lasers developed from di-octyloxy-paraphenylenevinylene (DOO-PPV) and derivatized DOO-PPV onto erbium doped optical fibers. A variety of differing solvent systems will be employed for the micro-ring forming polymer. The effect of ring formation from these solvents, with regard to the ring polymer morphology, will be thoroughly investigated using methods previously developed in our laboratories. Constituents added to the derivitized DOO-PPV to either enhance lasing action or render solubility will add a distinct “tunability” to the emission color of the laser. However, such additions may well affect general solubility as well as the final ring morphology which in turn may either enhance or diminish lasing action depending on the nature of the substituents. A direct result of this micro-ring work will be quantification of the emission and the necessary steps that will need to be taken to provide robust all organic fiber laser systems that are reproducible with ease of manufacturing.

Outreach to Industry:

Once we have a proof of concept amplifier using the OLED integrated onto the active optical fiber, we will begin to discuss options more fully with telecommunication companies such as Cisco, Corning, Lucent, and Fujikura. Fujikura donated the fiber that we are using in this proof of concept stage and will continue their interest.

New Resources Required:

Funds (\$10,000) will be requested for the upgrading of an existing gas chromatograph for better characterization of the PFCB monomers.

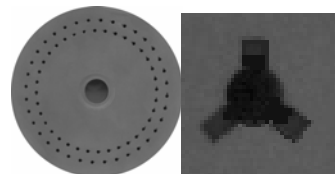


Figure 3a. A scanned image of the spinneret plate and a view of a single hole.

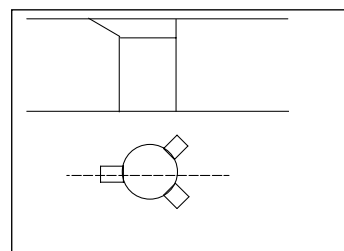


Figure 3b. A drawing of a single hole.