

## ~~Special Polymer Physics Seminar ~~

**Dr. Casey Check**

Department of Macromolecular Science and Engineering,  
Case Western Reserve University  
Cleveland, OH 44106

**10:00 AM Tuesday, February 15<sup>th</sup>, 2011**  
**301 Steidle Bldg.**

### **Design, Synthesis and Characterization of Two-dimensional Polyelectrolytes**

A novel two-dimensional poly(1,3,5-phenylene-4,4'-biphenylene-2,2'-disulfonic acid) (CPPSA) was synthesized using palladium-catalyzed Suzuki coupling in water. The postulated architecture is comprised of hexagonal, macrocyclic, 2-dimensional polymer sheets resembling a honeycomb. Such structures should exhibit a high driving force for 3-dimensional packing thereby creating materials with incompressible nano-channels which can retain water at very low relative humidity. Motivation for the design of such polymers is for use as significantly improved polymer electrolyte membranes for fuel cells.

A series of model compound studies based on monomer 4,4'-dibromobiphenyl-2,2'-disulfonic acid were performed to determine the optimal reaction conditions for cyclopolymerization. Emphasis was placed on evaluating water-soluble boronate compounds, bases, and ligands/catalyst systems in order to obtain quantitative yield of model compound quaterphenyl-2',2''-disulfonic acid. A kinetics model based off of the standard Suzuki coupling catalytic cycle was constructed to evaluate the rate of reaction based on the results of sampled model compound reactions.

Cyclopolymerization reactions were run under pseudo high-dilution conditions with slow monomer addition. The resulting polymers showed unusual physical properties including insolubility in water after condensing to the solid state. Subsequent ultrasonication with heating was shown to disperse the intractable solid polymers into "solutions" which could be used for film casting suggesting that their insolubility was due to aggregation and not from 3-dimensional crosslinking. Further supporting the postulated structural picture was the slow diffusion of water from CPPSA films into D<sub>2</sub>O in proton NMR experiments.

Imaging of the CPPSA polymers by scanning electron microscopy (SEM) indicated evidence of layered structures formed by extensive aggregation. Atomic force microscopy (AFM) showed further evidence of stacking of planar structures into larger assemblies. Clear evidence of hexagonal polymeric structures was observed by scanning tunneling microscopy (STM). Measurements of the lattice spacing indicate a void size of ~18 – 20.5 Å, which is consistent with the theoretical value based on bond-length calculations and molecular modeling (19 – 21.5 Å). These preliminary imaging results suggest that the desired hexagonal polymer structure was obtained.