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Project Title: Surface Modification of Polyaniline Films and Nanofibers with Polymer Brushes
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In the course of this project, we have demonstrated the use of controlled radical polymerization reactions to modify the surfaces of electrically conducting polymers with polyzwitterions, specifically poly(sulfobetaine metacrylate)(polySBMA), either in the form of thin films or as nanorods. While the surface modification reaction with thiols had been developed in our laboratories before the onset of this project, this work demonstrated our ability to do the reaction with initiators for the atom transfer radical polymerization (ATRP) reaction and to carry out that reaction on the conducting polymer surfaces. While we were concerned that the conducting polymer would suppress the reaction rates, we found that they were comparable or faster than those on gold surfaces when measured by the mass gain on a quartz crystal microbalance resonator (Fig. 1). The apparent rate acceleration is likely due to the increased roughness of the surface and the presence of a larger number of reactive sites.

During the first two years, we primarily worked with polypyrrole thin films and then with polyaniline nanorods. During year three, we expanded the scope of the work in several ways. First, we compared the results of the surface initiated reactions verse the “grafting to” reaction with polymers prepared in solution. We also extended our work

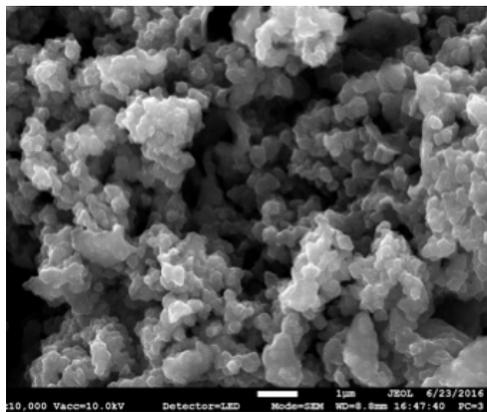


Figure 2: PEDOT nanoparticles after surface modification by poly(SBMA) through a grafting to process.

on nanoparticles to polypyrrole and poly((3,4-ethylenedioxythiophene)(PEDOT), demonstrating the versatility of the process. As observed with our earlier nanoparticle derivatization reactions, the surface modification (either grafting to or grafting from) reactions did not result in observable changes to the nanoparticle morphology (Fig. 2).

We chose to develop radical polymerization reaction that were operational in aqueous solutions rather than the more commonly used dry, air free organic conditions. This was one of the principle goals in the original proposal. We also developed routes to thiol-terminated polySBMA in solution, either using a solution phase ATRP reaction or a reversible addition-fragmentation polymerization (RAFT) reaction. In either case, the resulting polymers could be added to the conducting polymer surface and allowing for the comparison of the effectiveness of the two approaches.

In year three, we also began looking ahead at possible future applications of the nanoparticles. While we have demonstrated that we can alter the surface properties of conducting polymers, thin films are unlikely to be deployed on large surfaces or on surfaces that cannot be used as electrodes. The nanoparticles can be deployed but would require a matrix to hold them in place. So we have begun dispersing the particles in aqueous dispersions of polyurethane. These are related to commercial polyurethane paints, but we chose to make our own dispersions free of additives (colorants, antifungals, dispersants, etc.) that are typically present in commercial coatings.

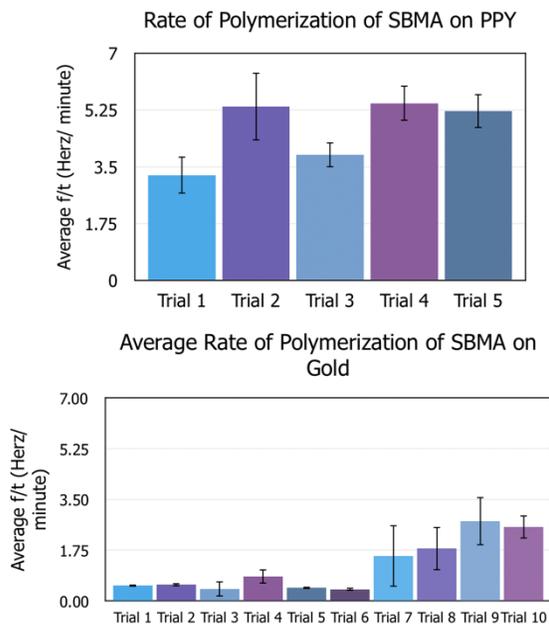


Figure 1: QCM frequency changes during surface-initiated ATRP polymerization to form polySBMA.

This project has directly supported six undergraduates over three years. Of these, four have entered graduate programs in chemistry and two are still enrolled at Furman. One of those will enter dental school next year and one is undecided. Other students were impacted by the project and have worked on related activities.



Figure 3: Polypyrrole nanoparticles derivatized with poly(SBMA) brushes dispersed in polyurethane to test dispersion, aggregation behavior and effect on matrix physical properties.