

## **4db Design, Synthesis, and Characterization of Functional Polymers, Surfaces, and Interfaces**

*Brandon M. Vogel*

### *Introduction*

My research interests focus on the design, synthesis, and characterization of functional polymers at surfaces and interfaces for applications ranging from controlled release of bioactive compounds to organic electronics devices. Powerful tools such as combinatorial characterization techniques, high-throughput synthesis, soft x-ray spectroscopy, and neutron scattering methods are utilized in investigations both fundamental in nature and directed towards specific technologies. Completed projects include the synthesis of a model platform to study polymer erosion, the design and optimization of a parallel micro-dissolution apparatus, and the systematic investigations of interfacial chemistry on the material microstructure and electrical performance of organic field effect transistors.

### *Polyanhydride-based Libraries for the Controlled Release of Bioactive Molecules*

Polyanhydrides are an important class of hydrolytically degradable biomaterials for controlled release applications. They are ideal candidates to stabilize biomacromolecules such as therapeutic proteins, vaccines, and growth factors because they exhibit surface erosion behavior. However, polyanhydrides are limited by poor processability, low solubility in common solvents, and their hydrophobicity. Moreover, choosing a copolymer composition that can effectively stabilize a given therapy is not trivial and is complicated by a large parameter space. For instance, factors to consider for a controlled release device are polymer degradation, drug release kinetics and therapeutic stability. We addressed these challenges by 1) developing a model bulk eroding polyanhydride by the addition of ethylene glycol segments to the monomers and 2) developing high throughput microwave polymerization, parallel library synthesis and characterization methods for polyanhydride copolymers. Copolymers were synthesized to tailor the hydrophobicity of the polyanhydride, tune the solubility of molecules within the polymer, and vary the polymer degradation rate. Moreover, since these oligoethylene glycol homopolymers undergo bulk erosion, copolymers with other anhydride monomers allow the study of the fundamental nature of the erosion process without changing chemistries. Following the high-throughput synthesis of different copolymer compositions, a parallel microdissolution measurement device was developed using a lithographic rapid prototyping process. The device (2" by 3" dimensions) was used to measure simultaneously the release kinetics of twenty-five copolymers.

### *Effect of Chemically Modified Dielectric Interfaces on Semiconducting Polymer Chain Orientation*

Conjugated organic semiconductors such as poly(3-hexylthiophene) (P3HT) have shown promise for use in applications such as flexible display technology and radio frequency identification tags. Unlike inorganic materials, organic device performance is strongly dependent on the structure and properties of the interfaces between materials. However, a clear understanding of the effect of interfacial properties on the structure and electrical characteristics of the polymer, however, remains incomplete. We employ two strategies to vary the interfacial chemistry to clarify the influence of either surface energy or chemical functionality on the chain orientation of P3HT. First, linear surface energy gradients were prepared by systematically oxidizing several aliphatic silane chemically modified surfaces with a UV ozone lamp. P3HT was spin coated on top of these substrates and the polymer axis tilt was determined using Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy. We find a weak dependence of chain orientation on substrate surface energy and some dependence on the aliphatic surface functionality. Second, the chemical functionality at the polymer monolayer-interface was modified using a versatile monolayer chemistry based on isocyanate-amine chemistry. This strategy allows the production of monolayers with aromatic functionality such as thiophene, fluorine, and pyridine surfaces.

P3HT exhibited varying levels of orientation depending upon the monolayer chemistry and the solvent from which the polymer was spin coated, even for surfaces with the same water contact angle. These results suggest that specific interfacial chemical interactions as well as the film formation variables (casting solvent) can strongly influence the polymer conjugated plane tilt.

## References

### JOURNAL ARTICLES:

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2. **B.M. Vogel**, Naomi Edelman, S.K. Mallapragada and B. Narasimhan, "Parallel Synthesis and Dissolution Testing of Polyanhydride Random Copolymers", Submitted to the Journal of the American Chemical Society, March (2005).
3. **B.M. Vogel** and S.K. Mallapragada, "Synthesis of Novel Biodegradable Polyanhydrides Containing Aromatic and Glycol Functionality for Tailoring of Hydrophilicity in Controlled Drug Delivery Devices", *Biomaterials*, 26, 721-728 (2004).
4. S. Lin-Gibson, S. Bencherif, J.A. Cooper, J.M. Antonucci, **B.M. Vogel**, and N.R. Washburn, "Synthesis and Characterization of PEG Dimethacrylates and their Hydrogels", *Biomacromolecules*, 5, 1280-1287 (2004).
5. **B.M. Vogel**, S.K. Mallapragada, and B. Narasimhan, "Rapid Synthesis of Polyanhydrides By Microwave Polymerization", *Macromolecular Rapid Communications* 25, 330-333 (2004).

### BOOK CHAPTERS:

1. **B.M. Vogel** and S.K. Mallapragada, "The Synthesis of Polyanhydrides", in *Handbook of Biodegradable Materials and their Applications*, edited by S.K. Mallapragada and Balaji Narasimhan, Volume 1, 1-19 (2005).

The surfaces and interfaces of polymer films impact many properties including adhesion, printability, barrier performance, appearance and strength. Much of the value of converted polymer products revolves around surface modification and coatings. The thickness of these layers can range from the sub-nanometer -for contaminants or corona treatments - to tens of microns for packaging, paints and laminates. Figure 14 shows a molecular depth profile of a specially designed test specimen made from alternating thin and thick organic layers deposited on a silicon wafer. TOF-SIMS with GCIB profiling is able to maintain the molecular signal from the two different Irganox molecules as a function of depth. XPS is a surface sensitive analytical tool for probing surface chemical phenomena on polymers. The structural characterization of as-synthesized preceramic polymer precursor was investigated by FT-IR and NMR. Thermal degradation was studied by TGA. First, the design of the precursors could lead to three different possibilities in the final ceramics: (i) the final ceramics without free carbon ( $y=0$ ) are prepared using precursors containing together with Si-R (alkyl groups) also Si-H and Si-Si bonds; [25,26] (ii) SiOCs with a low amount of free carbon if Si is bonded to alkyl group such as. In the literature, several studies focusing on the synthesis and characterization of SiOCN systems have been reported. [73,74]. SiOCN ceramics can be obtained via pyrolysis of the polymer precursors which are generally prepared from two main synthetic routes. The Special Issue of "Functional Surfaces/Interfaces Enabled Smart Behaviour in Soft Matter System and Their Engineering Applications", will focus on the emerging, interdisciplinary smart materials and surfaces technologies with a focus on developing a fundamental understanding of the fabrication and formation of novel surface/interfaces, complying with structure-property relationships and functions that will lead to wide impacts in future engineering applications. A collection of original/review papers will be scoped with focusing on the recent progresses on: (a) Design and fabrication of smart functional surface and thin films; (b) multiscale morphological transformation enable robotic structure; (c) surface and interface driven...