Thin Film Division
Room A105 - Session TF-ThA

Organic and Polymeric Materials

Moderators: Mark Losego, Georgia Institute of Technology, **Matthias Young**, University of Missouri

2:20pm **TF-ThA-1 Chemical, Biological, and Topological Control Using Chemical Vapor Deposition Polymerization***, **Joerg Lahann**,* University of Michigan, Ann Arbor **INVITED**

Chemical vapor deposition (CVD) polymerization is a highly effective method for producing conformal, defect-free, and precisely adjustable organic thin films. CVD is particularly advantageous for barrier coatings due to its ability to eliminate the environmental, health, and safety risks associated with solvents, while also providing a wide range of post-polymerization modification options. In this presentation, I will discuss the use of poly-p-xylylene (PPX) and its functional derivatives for modifying the chemical and biological properties of surfaces.

Beyond film deposition, anisotropic liquids, such as liquid crystalline (LC) phases, offer an intriguing possibility for templating materials due to their unique long-range alignment and elastic properties. By combining the benefits of CVD with LCs, we were able to synthesize end-attached nanofiber arrays supported by a solid surface using LC-templated CVD polymerization. Upon rinsing the LC template with organic solvents, we observed that the alignment of the resulting nanofibers correlated with the molecular ordering of the LC template. For example, when a nematic LC film with homeotropic (vertical) anchoring to the substrate was used, the resulting nanofibers were straight, whereas a cholesteric LC film induced helical nanofibers. We further manipulated the morphology of the nanofibers to form enantiomerically pure nanohelices by using a precursor with a chiral center.

T.M. Hafshejani, X. Zhong, J. Kim & J. Lahann, Chemical and Topological Control of Surfaces using Functional Parylene Coatings. *Organic Materials* **2023**, (in press).

X. Zhong, R. Jordan, J.-R. Chen, J.E. Raymond, J. Lahann, Mechanistic studies into the area-selectivity of chemical vapor deposition polymerization, *ACS Applied Materials and Interfaces* **2023** (in press).

D. Varadharajan, K. Nayani, C. Zippel, E. Spuling, K.C. Cheng, S. Sarangarajan, S. Roh, J. Kim, V. Trouillet, S. Bräse, N.L. Abbott, J. Lahann, Surfaces decorated with enantiomorphically pure polymer nanohelices via hierarchical chirality transfer across multiple length scales, *Advanced Materials* **2022**, 34, 2108386.

K.C.K. Cheng, M.A. Bedolla-Pantoja, Y.-K. Kim, J.V. Gregory, F. Xie, A. de France, C. Hussal, K. Sun, N.L. Abbott, J. Lahann,Templated Nanofiber Synthesis via Chemical Vapor Polymerization into Liquid Crystalline Films, *Science* **2018**, 362, 804–808.

3:00pm **TF-ThA-3 On the Mechanism of Oxidative Molecular Layer Deposition***, **Matthias Young**, Q. Wyatt, K. Brathwaite, M. Mehregan, M. Ardiansyah, N. Paranamana, K. Brorsen,* University of Missouri

Oxidative molecular layer deposition (oMLD) was first reported in 2014 to form poly(3,4 ethylenedioxythiophene) (PEDOT) thin films using sequential gas-phase exposures of ethylenedioxythiophene (EDOT) monomers and an $MoCl_5$ chemical oxidant. In the last few years, the number of oMLD polymer chemistries has expanded to include at least four additional monomers, with successful demonstrations using at least three different chemical oxidants. These advances have laid the foundation for oMLD to potentially access a large library of polymers and copolymers with molecular-level precision of thickness and composition. However, within this broad landscape it has been unclear which polymer chemistries will and will not be accessible by oMLD. Here, we report on work to establish fundamental insights into the oMLD growth mechanism to guide further oMLD research. We examine oMLD growth using EDOT, pyrrole (Py), paraphenylenediamine (PDA), thiophene (Thi), and furan (Fu) monomers. We specifically identify (a) the importance of surface monomer-oxidant complexes that lead to self-limiting oMLD surface reactions and (b) the necessity for a two-electron chemical oxidant in these reactions, which must have sufficient oxidation strength to oxidize both a surface and a gas-phase monomer to enable oMLD growth. The mechanistic insight from these studies provides a conceptual framework to predict which oMLD chemistries are accessible using current known oxidants and identify opportunities to develop new chemical oxidants to access a broader range of oMLD chemistries.We report on studies testing the limits of these mechanistic principles by examining oMLD of various monomers and oxidants, as well as oMLD of copolymers. Interestingly, we also identify that molecularly assembled copolymer structures formed by oMLD provide improved electrochemical properties over the corresponding isolated homopolymers. The insights from these studies (1) help establish a roadmap for promising future directions in oMLD research, (2) provide a pathway to address previously intractable questions regarding the molecular origins of polymer properties, and (3) provide an opportunity to control and optimize polymer structure and properties for electrochemical applications including energy storage, water desalination, and sensors.

3:20pm **TF-ThA-4 Adsorbed Polymer Crystals in Icvd: Prevention and Control***, **Simon Shindler**, R. Yang,* Cornell University

Initiated chemical vapor deposition (iCVD) is a technique used to fabricate polymer thin films from the vapor phase. For most applications, films produced in iCVD are practically defect free. However, as the technique is used more often in precision applications like membrane synthesis and even at an industrial scale, quality control and defect prevention will become critical. In this study, we address an important knowledge gap in iCVD by investigating defect formation, a topic that has received little attention to date. We show for the first time that polymer chains which accumulate in the reactor during normal operation can cause defects by forming aggregates on the sample surface. To study these defects in a controlled environment, we mimic the conditions under which they form. Nucleation and growth of defects are measured using optical microscopy over a range of temperatures and in the presence and absence of adsorbed monomer to better understand what drives aggregation. With this understanding we propose a method by which aggregates (and by extension, defects) can be prevented without restricting the domain of potential deposition conditions or stage temperatures used. Our investigation provides a better understanding of the factors driving polymer aggregation in iCVD, which may lead to further improvements in the deposition process.

3:40pm **TF-ThA-5 Area-Selective Initiated Chemical Vapor Deposition (AS-iCVD) for Non-Lithographic Patterning of Polymer Thin Films***, **Junjie Zhao**[1],* Zhejiang University, China

Patterning of polymer thin films is key to device fabrication and surface engineering. Developing non-photolithographic strategies such as area selective deposition (ASD) could bypass the need for complex optical systems and provide versatile routes for producing polymeric nanostructures. While previous attempts to achieve area selectivity for condensation polymerization and ring-opening metathesispolymerization have been reported, strategies are yet to be explored for initiated chemical vapor deposition (iCVD) which involves free radical polymerization. In this talk, we will present a plasma surface treatment method to enable area-selective initiated chemical vapor deposition (AS-iCVD) for poly(1,3,5-Trivinyl-1,3,5-trimethylcyclotrisiloxane) (pV_3D_3). Using HBr/Ar and O_2 plasma, we were able convert Cu regions to high oxidation states, creating radical inhibitors in the non-growth area for iCVD. Our plasma surface treatment resulted in a nucleation delay of ca. 30 min, and enabled a deposition selectivity of ca. 90% on SiO_2 surface. We will discusshow plasma processing time affects the composision of surface Cu species and the resulting area selectivity for iCVD pV_3D_3.We will also show the application of our AS-iCVD process to pre-patterned Cu/SiO_2 substrates as a demonstration for self-aligned polymer patterning.

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[1] **TFD Paul Holloway Award Winner**

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