Analysis and Characterization of 2D Polyaramids

by

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Polymers that extend covalently to form a two-dimensional lattice, one atom in thickness, are promising materials in that they combine the mechanical strength, barrier properties, and in-plane conduction of 2D nanomaterials such as graphene, hexagonal boron nitride, and molybdenum disulfide, with the low density, chemical tunability, and solution processability of conventional organic polymers. Previously thought to be impossible to synthesize in the solution phase, the Strano laboratory at MIT demonstrated the first irreversible polycondensation to 2D polymer aramid, labeled 2DPA-1 or 2D polyaramid-1. The resulting discoidal platelets between 2 to 26 nm in diameter self-assemble via intermolecular amide hydrogen bonding into highly oriented, tightly packed nanofilms upon spin-coating. While all existing 1D polymers exhibit some measure of gas permeability through the free volume of entangled chains, 2DPA-1 is the first organic polymer to be molecularly impermeable to small molecule gases. Despite this promise, 2D polyaramids are like their 1D polyaramid counterparts in having limited solvent solubility, and are otherwise incompatible with chromatographic and other methods of characterization. This thesis addresses this major hurdle to the understanding and synthesis of this class of materials by developing a series of new techniques to characterize 2D polyaramids in the solution and solid-state phases.

The 1H-NMR analysis of the aromatic and proton end groups of 2D polyaramids in solution can yield a measure of molecular weight and discoidal size, while the skewness of the aromatic region provides a relative weighting between dendritic, small, and larger polycyclic domains, linked directly to graph theory representations of these macromolecules. Building onto this, Diffusion-Ordered NMR Spectroscopy (DOSY) can yield a chromatographic-like molecular distribution without physical separation, also by probing the 1H nuclei. Herein, I develop novel tools using DOSY to measure the size distribution of such molecules. I address the difficulty of interpreting diffusion NMR experiments due to the mathematically ill-posed nature of the requisite transform, noting that existing Inverse Laplace Transform (ILT) algorithms produce physically inconsistent outputs when applied to 2D polyaramids. I develop two pre-ILT analysis methods. The first is the diffusion trajectory, which I use to analyze the DOSY spectra directly, mapping the aromatic-to-end-group ratio r against the spectral skewness s of the aromatic region. The second solves for the Sparse Transform, a limit that represents diffusing species as having a delta-function representation in ILT space. I also introduce the Model-based Inverse Spectral Simulation Transform (MISST), which incorporates prior knowledge of 2DPA-1 spectral properties to recover lognormal platelet size distributions satisfying this benchmark, outperforming commercially available algorithms including PALMA on larger-platelet samples. These tools generalize beyond 2DPA-1 to any polydisperse nanomaterial for which NMR spectral properties can be simulated as a function of size.

As spin-coated nanofilms, 4 to 65 nm thick, 2DPA-1 exhibits nitrogen permeability below 3.1×10^{-9} Barrer, nearly four orders of magnitude lower than the least permeable conventional polymers and approaching the H_2 permeability of pristine monolayer graphene. I attribute this

to staggered AB-stacking of successive platelet layers, which offsets unit-cell pores between adjacent layers and eliminates any continuous transmembrane pathway. For ultra-low permeability measurements, the nanofilm bulge test platform suspends thin films over etched microwells and monitors deflection under gas pressure. It is highly sensitive but conventionally limited to static atomic force microscopy (AFM) measurements under near-atmospheric conditions. I developed an interferometric deflection algorithm that converts visible light interference patterns into nanoscale height information using a standard optical microscope. This extends the platform to dynamic pressurization, elevated temperatures, and chemically demanding environments inaccessible to AFM. Applying this technique, I directly observed the gas filling and sealing behavior of 2D polyaramid nanofilm bulges in real time, providing the first evidence of mechanosensitive rim seal opening and resealing and validating our measurement of nitrogen impermeability. To establish long-term durability, I monitored 2DPA-1 nanofilm bulges continuously for over 1000 days. Day-to-day deflection fluctuations follow a confined random walk whose confinement length scales with initial bulge volume ($R^2 > 0.96$), a relationship that holds across different bulge geometries and materials including graphene. Thermal cycling to 120°C produces fully reversible deflection changes with no measurable gas loss, confirming the rim seal remains intact throughout. This multi-year integrity rules out both hygroscopic degradation and physical aging as failure modes.

In total, the work of this thesis introduces and benchmarks several new characterization methods for 2D polyaramids that should find wide utility for 2D polymers broadly, opening pathways to scalable barrier coatings, separation membranes, and nanoelectromechanical devices that were previously constrained by the incompatibility of atomic-scale impermeability with solution processing.

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