Chemical Engineering Dissertation Defense

Understanding the Crystallinity-Structure-Property Relationships in Crystalline Polymeric Materials for Enhanced Applications via Novel Characterization Techniques

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Abstract

Crystalline polymeric materials play an increasingly important role in daily life. Understanding and controlling the development of crystallinity is integral to improving the performance of crystalline polymers in packaging, drug delivery, water treatment, gas separations, and many other industries. Herein, fluorescence and Raman spectroscopy have been applied for the first time to study the crystallinity of polymers, including traditional semicrystalline thermoplastics and covalent organic frameworks (COFs; an emerging class of crystalline polymers with highly ordered pore structures). On one hand, by incorporating a fluorescent dye segment into a semicrystalline polymer matrix, it is feasible to accurately monitor its crystallization and melting. The flexibility of dye incorporation allow for new fundamental insights into polymer crystallization in the bulk and at/near interfaces that may otherwise be out of reach for established techniques like differential scanning calorimetry (DSC). On the other hand, Raman spectroscopy has been identified as a technique sensitive to the crystallinity of COFs and applied alongside well-established characterization techniques (X-ray diffraction and N2 adsorption) to monitor the crystallization of COFs during synthesis. This has enabled careful control of COF crystallinity during solvothermal synthesis for improved application in the field of drug delivery. The monitoring of COF crystallinity has been extended to more complex film geometries produced by interfacial polymerization. The high molecular sieving potential of COFs remains out of reach in part due to a lack of understanding of the interplay between crystallinity, crystallite orientation, and filtration performance. A careful study of these relationships is suggested for future work to provide key insight toward applying COFs as molecular sieving materials in water treatment and other separation applications.

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