**Thermal FFF and LC for Polymers of High Molecular Weight and Complex Architectures**

**Background and significance:** Many natural polymer products are used in food, beverage, and cosmetic applications, and many synthetic products have applications such as adhesives for electronic materials, woodworking, pressure sensitive adhesives, and laminations. To meet the needs of such a diverse product environment, existing and future products require a wide range of polymer architectures and microstructures. Different architectures include polymer gels (crosslinked), and ultrahigh molecular weight polymers (greater than $10^7$ Daltons) to very low molecular weight polymers ($10^3$ Daltons and below). In addition, other polymer architectures in commercially interesting polymers include randomly branched polymers, radial (star) polymers, and grafted, block, and random copolymers as well as mixtures of these architectures. The physical properties are profoundly impacted by the degree of branching in randomly branched polymers, number of arms in radial polymers, grafting density in grafted polymers, and the blockiness and randomness of copolymers. Microstructural differences also impact the physical properties of polymers. In commercial materials of these types, mixtures of architectures and microstructures are inevitable. Therefore, the ability to effectively separate and characterize materials based on both polymer architecture and microstructure is key to understanding existing product performance and effectively developing new products.

Gel permeation chromatography (GPC) is widely used to separate polymers. However, it has many fundamental limitations; the main ones being 1.) the sample is usually pre-filtered to remove components that may plug the column. Hence, information about microgels cannot be obtained. In addition, it has been demonstrated that the filtration process also removes a significant portion of lower MW soluble polymers. 2.) the GPC system separates polymers by molecular size only. Hence, polymers with different architectures (branching, grafting, composition, etc.) cannot be chromatographically differentiated. 3.) GPC columns have a limited molecular weight range. In addition, ultrahigh MW polymers are prone to shear degradation as they navigate through the narrow interstices present in packed columns.

**Thermal FFF Goals:** Our research aims to transform an under-used technique, thermal field-flow fractionation (ThFFF), into a cornerstone technology for separating and characterizing complex polymer architectures. ThFFF has been used for polymer analyses despite an incomplete understanding of the thermal diffusion effect that gives the technique its unique separations capabilities. Central to this work is the establishment of trends and mathematical relationships between thermal diffusion coefficients and polymer
properties (molecular weight, composition, architecture) in various solvents. This can be achieved by performing an extensive study in which different combination of solvents (pure and binary), polymers, and polymer architectures (linear, random, block, and grafted copolymers) are systematically varied. Insights gained from these fundamental studies with well characterized standards will be subsequently used to analyze industrially important classes of polymer materials, e.g., pressure sensitive adhesives, block co polymers, and starch. This work will pave the road to detailed correlations of polymer properties and performance and should stimulate theoretical development and increased understanding of polymer thermophoresis.

**Goals for Liquid Chromatography Studies:** We are investigating “novel” polymer separation techniques such as liquid chromatography with monolithic columns, gradient polymer elution chromatography, and critical adsorption chromatography. These techniques have been demonstrated to yield unique information on end groups and sequence length distributions in copolymers. The question we are trying to answer is how well these methods work in the analyses of industrially important classes of polymers.

The objectives of this program are to apply emerging separation technologies for polymer separations to establish optimal separation techniques for analyzing polymers, singly and as mixtures, according to their differing architectures. The study will establish “best practices” for separating and fully characterizing the wide range of polymer architectures relevant to industry. Some of our aims include separating 1.) polymer gels from soluble polymers in emulsions and characterize both materials, 2.) radial polymers by the number of arms in order to fully characterize the branching, 3.) ultrahigh molecular weight polymers by composition differences, and 4.) grafted polymers by grafting density and composition drift.

**Educational benefits:** This project gives students the rare opportunity to work closely with industrial scientists and to experience the industrial perspectives.