Contribution ID: **117** Contribution code: **Board 13** Type: **Poster Presentation**

Quantification of Copolymer Microstructure from Liquid Chromatography using a Statistical Interaction Model

Monday, May 20, 2024 7:10 PM (20 minutes)

Copolymers have a microstructure defined by their constituent monomers' sequence. This microstructure can have a wide-ranging impact on its structure-function properties and is often difficult to control during polymerization, thus is crucial to understand. Quantification of synthetic copolymer microstructure is challenging due to the large heterogeneity of molecular species and the limited classes of analytical instrumentation available to study high molecular weight molecules. Polymer chromatography is an attractive technique due to its ability to capture distributed properties, and tune separation selectivity for molecular weight (i.e. chain length) or monomer chemistry. It is performed using the broad tools of high-performance liquid chromatography (HPLC), but with careful attention paid to the thermodynamics of the polymer-solvent-porous substrate interaction. The most common application of polymer chromatography is size exclusion chromatography (SEC), where enthalpic interactions are minimized and the resulting separation is driven by the entropic tendency of large molecules to avoid small pores. This results in a separation by solute size and is the standard approach to quantify a polymer's molecular weight distribution.

Other experimental situations are possible. For example, if a solvent-substrate pair is selected to approximately balance entropic exclusion and enthalpic adsorption, the retention effects of chain length can be muted. This phenomenon is called the critical point of adsorption (CPA) and has been shown to be sensitive to copolymer composition and microstructure [1]. The elution of polymers can be modelled in these conditions with a relatively simple interaction model [2], which was extended numerically to more complex polymers [3]. This work further extends these approaches to a real-world characterization problem: assessing and monitoring the transesterification of a novel polyester with PET. This was accomplished by including a Markov Chain model to describe the copolymer microstructure [4] and development of suitable chromatographic and spectrographic conditions. We show that the degree of transesterification can be quickly and accurately assessed using these methods. Further, we show how this approach is applicable to any copolymer system that elutes at a CPA.

References:

1. Y. Brun; C.J. Rasmussen. Chapter 11 –Interaction Polymer Chromatography. In: S. Fanali, P.R. Haddad, C.F. Poole, M.-L. Riekkola, editors. Liquid Chromatography (Second Edition); Elsevier, 2017 p. 275–318.
2. Y. Brun; Peggy Foster. Characterization of synthetic copolymers by interaction polymer chromatography: Separation by microstructure; J. of Separation Science, 33 (2010) 3501–3510.
3. C.J. Rasmussen. Molecular Simulation of Simple Fluids and Polymers in Nanoconfinement. Doctoral dissertation, Rutgers, The State University of New Jersey. ProQuest Dissertations Publishing, 2012.
4. F.P. Price. Copolymerization Mathematics and the Description of Stereoregular Polymers; J. Chem. Phys., 36 (1962) 209–218.

Primary authors: RASMUSSEN, Christopher (Bolt Threads Inc.); Dr BRUN, Yefim (International Flavors and Fragrances)

Presenter: RASMUSSEN, Christopher (Bolt Threads Inc.)

Session Classification: Poster Session

Track Classification: Poster Presentations