Controlled polymerizations are highly sought-after methods for preparing macromolecules since they have the potential to produce large molecules with consistent length, sequence, and end groups. In this vein, much of our work has focused on the implementation of ‘living’ methods to produce new classes of very well-defined conjugated polymers. In particular our group has utilized the Kumada Catalyst Transfer Polymerization, which was pioneered by the Yokozawa and McCullough groups, to prepare new classes of well-defined conjugated polymers including those that incorporate ‘heavy’ atoms such as selenium and tellurium. Very recently we have learned two remarkable things about this exciting polymerization method. In one line of inquiry, I will describe how we are able to arrest the catalytic cycle at the transmetalation step by controlling the temperature. This allows us to ‘stop’ the polymerization and add stoichiometric amounts of monomer one by one. In doing so, we are able to prepare monodisperse polymers of poly-3-hexylthiophene (P3HT) in a homogeneous manner. In a second line of inquiry, I will show that after reductive elimination and oxidative addition the catalyst-polymer complex is remarkably stable. This allows us to isolate pure living chains with the polymerization catalyst intact at the chain ends and still active. While these are both remarkable feats in polymer synthesis, they are limited in monomer/catalysts scope to P3HT and P3HT-like systems. In the final part of this talk, I will discuss a new initiative in our group to use templates to prepare broader classes of well-defined conjugated polymers.

Selected References:

Pahlavanlu, Seferos and coworkers. Polymer Chem. 2021, 21, 511-518.

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