

## An Organocatalytic Approach to Polyester Synthesis

Partha Datta

Kiesewetter Lab Group

Organic catalysts have been used in synthesis for more than a century. However, the application of these organic catalysts in polymer synthesis has only occurred since the turn of the century. Hedrick and Waymouth initiated the field of hydrogen-bonding organocatalysts in the manufacturing of polyesters circa 2005.<sup>1,2</sup> This class of catalyst is typically employed as a bimolecular cocatalysts pair consisting of an H-bond donor and H-bond accepting base. Although the focus was initially on the synthesis of polylactones, the scope of monomers continued to expand over the last few years. Detailed mechanistic investigations also provided an understanding of binding events which give rise to the polymerization.<sup>3</sup> While the exact mode of activation is still under study, a cooperative or anion-mediated pathway is believed to transpire for the polyester synthesis, depending on the cocatalyst pair used and their acidity. Due to the excellent control over reactivity, rate and selectivity with these organocatalysts, mainly ureas and thioureas, polymers from some of the underexplored monomers became possible. It is with this ambition that we embarked on the sulfur-containing lactones which previously demonstrated poor control in polymerization with metal-based catalysts. However, with the advent of organocatalysts, this challenge was possible to overcome for these monomers. Following the successful ring-opening polymerization (ROP) of  $\epsilon$ -thiocaprolactone, we focused on the other thionated derivative,  $\epsilon$ -thionocaprolactone.<sup>4,5</sup> Applying the same principle of dual activated H-bonding catalysis, we were able to produce well controlled, monodisperse polythioesters. Due to the 'living' characteristics of this polymerization, we were able to produce a range of copolymers with tremendous control and remarkable properties. This allowed for the extension of these thionolactones to some of the less explored macrolactones. These new materials are being studied from a thermal and mechanistic perspective, to shed light on their future applications.

1. Nederberg, F.; Connor, E.F.; Moller, M.; Glauser, T.; Hedrick, J.L. New Paradigms for Organic Catalysts: The First Organocatalytic Living Polymerization. *Angew. Chem. Int. Ed.* **2001**, *113*, 2784-2787.
2. Dove, A.P.; Pratt, R.C.; Lohmeijer, B.G.G.; Waymouth, R.M.; Hedrick, J.L. Thiourea-Based Bifunctional Organocatalysis: Supramolecular Recognition for Living Polymerization. *J. Am. Chem. Soc.* **2005**, *127*, 13798-13799.
3. Kazakov, O.I.; Datta, P.P.; Isajani, M.; Kiesewetter, E.T.; Kiesewetter, M.K. Cooperative Hydrogen-Bond Pairing in Organocatalytic Ring-Opening Polymerization. *Macromolecules.* **2014**, *47*, 7463-7468.
4. Bannin, T.J.; Kiesewetter, M.K. Poly(thioester) by Organocatalytic Ring-Opening Polymerization. *Macromolecules.* **2015**, *48*, 5481-5486.
5. Datta, P.P.; Kiesewetter, M.K. Controlled Organocatalytic Ring-Opening Polymerization of  $\epsilon$ -Thionocaprolactone. *Macromolecules.* **2016**, *49*, 774-780.