

## Fundamental Research in Organocatalytic Ring-Opening Polymerization: A Trek to New Catalysts

Oleg I. Kazakov

Department of Chemistry, University of Rhode Island

The slate of H-bonding cocatalysts stands out among the larger class of organocatalysts for ring-opening polymerization (ROP) for their ability to yield polyesters with precisely controlled properties. These cocatalysts are believed to operate by H-bond activation of monomer by an H-bond donor, commonly a thiourea, and by activation of alcohol chain end by base. The activity of the cocatalyst pair varies with the identity of the base cocatalyst. For a set of structurally diverse base cocatalysts in combination with thiourea, the strength of the binding between the cocatalysts in solution relates to the activity of the cocatalyst pair. The varied activity of structurally similar bases in the thiourea plus alkylamine cocatalyzed ROP of lactide tested the limits of this correlation. However, chemical kinetics investigations performed in the course of these studies inspired the development of new, highly effective, H-bonding thiourea catalysts for ROP. The success of the emerged catalytic systems allowing to dramatically increase the ROP rate led to modifications of the H-bonding catalysts in an attempt to effect stereoselective ROP – a challenging, yet teeming with synthetic prospects, focus area for organocatalysis.