

H-bonding catalyst systems for the ROP of cyclic esters.

Timothy Bannin

Organocatalytic ring-opening polymerization (ROP) is a widely-used method for creating highly functionalized polymers. Organocatalytic ROP exhibits precise control over molecular weight, narrow polydispersity index (PDI), and high functional group tolerance. Various H-bonding mediated organocatalytic systems, (thio)urea and H-bond accepting base, are applied to the ROP of ϵ -thiocaprolactone (ϵ -tCL), ϵ -caprolactone (ϵ -CL), and δ -valerolactone (δ -VL). By changing the (thio)urea from a singular moiety to one that contains multiple hydrogen bond donating (thio)ureas increases the rate and control of the system. However, applying a dual moiety base (bn-bisTBD) to the ROP of ϵ -CL and δ -VL does not increase control over the system. The presence of high concentrations of the H-bond accepting base MTBD (500 mM) causes the reaction to slow dramatically. When the thiourea is exchanged for the less acidic, commercially available, urea an increase in rate is observed even in H-bond disrupting solvents.