

Synthesis of electron-deficient borinic acid polymers and their applications in supramolecular assembly and as catalysts in amide bond formation

Monika K. Baraniak¹, Roger Lalancette², Frieder Jaekle²

1. Chemistry, Rutgers University-Newark, Wayne, NJ, United States.
2. Department of Chemistry, Rutgers University - Newark, Newark, NJ, United States.

The enhanced Lewis acidic character of borinic acid -functionalized polymers suggests broad potential applications in supramolecular materials, chemo- and biosensors, as well as supported catalysts. This presentation will discuss the synthesis of a new class of more electron-deficient borinic acid polymers, studies on their supramolecular assembly, and investigations into their use as catalysts in amide bond formation. We synthesized two electron-deficient borinic acid copolymers poly(styrene-co-2,4-dichlorophenyl borinic acid) and poly(styrene-co-3,5-dichlorophenyl borinic acid). Due to the less bulky and more electron-withdrawing group at the boron center these polymers are able to form supramolecular assemblies via Lewis acid – Lewis base interactions and reversible covalent B-O-B bond formation. The dynamic processes were studied in detail by variable temperature (VT) NMR using 2,4- and 3,5-substituted (dichlorophenyl)(*tert*-butylphenyl)borinic acids as molecular model compounds and the respective pyridine-complexed boroxanes, R'RB-O-BRR'(Py). The polymers and their corresponding model compounds were also examined as catalysts in the amide bond formation reaction between phenylacetic acid and benzylamine. The 3,5-dichlorophenyl borinic acid derivatives proved to be the more effective catalysts. Mechanistic studies suggested that the borane Lewis acid-catalyzed coupling involves initial acid-induced protodeboronation to release the dichlorophenyl boronic acid as the active catalyst.

