Coordination Polymerization Behavior of Various Unsaturated Monomers by Highly Active Nickel Catalysts Derived from 2,6-Dihydroxybenzoate

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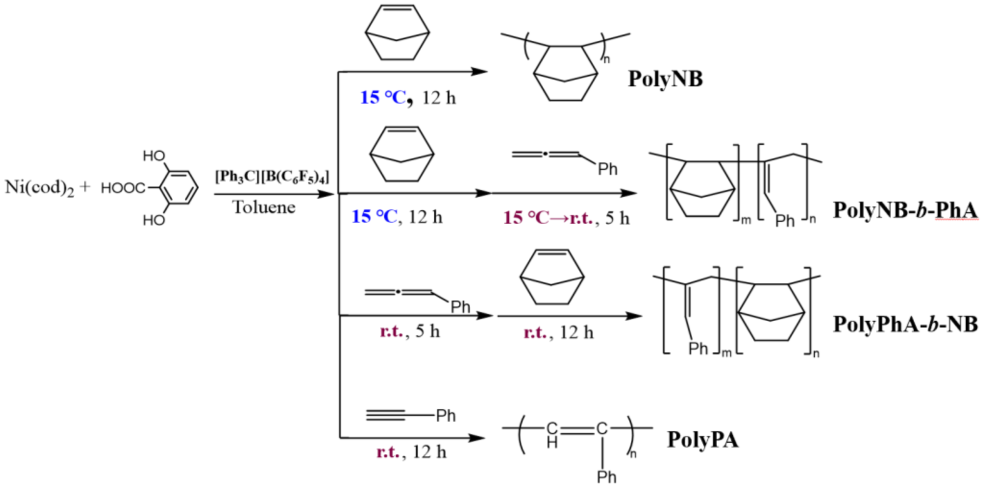
Keywords: *Coordination polymerization, Nickel catalysts, Unsaturated Monomers, Norbornenes, Acetylene Derivatives*

Coordination polymerization of unsaturated monomers such as norbornene (NB), allene, diene, and acetylene derivatives have drawn attention due to the excellent performance and functions of the resulting polymers suitable for versatile applications. For example, polynorbornene features a rigid cyclic structure with excellent thermal stability and optical properties, polyacetylenes with rigid π-conjugated backbones provides optoelectronic functions, and so on.[1,2] Accordingly, catalyst systems capable of conducting the coordinating polymerization of various unsaturated monomers holds significant industrial and scientific implications.

We have described that the nickel-catalyzed living coordination polymerization of allenes can produce well-defined polymers containing various functional groups.[3] Additionally, nickel catalysts bearing 2,6-dihydroxybenzoate ligands efficiently accelerate the living coordination polymerization.[4] Herein, on the basis of the highly active nickel catalysts, we described the polymerization of NB and the copolymerization of NB and phenylallene (PhA) in the presence of a small amount of co-catalysts such as $[Ph_3C][B(C_6F_5)_4]$ (Scheme 1). The living polymerization of NB can take place accompanying the nice control of the molecular weight even with larger amounts of NB (500~1000 equiv.) to produce polymers in high yields (Scheme 1). Further, the block copolymers of NB and PhA were obtained effectively through a living mechanism irrespective of the order of monomer additions. The polymerization behavior of other unsaturated monomers such as acetylene derivatives will also be described.



Scheme 1 Coordination (co)polymerization of unsaturated monomers by Highly Active Nickel Catalysts

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