Extending the livingness of Pd-catalyzed vinyl addition polymerization of norbornenes through mechanism-guided optimization

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The living vinyl addition polymerization of norbornenes is a robust method for accessing high molecular weight, solvent processible materials with a chemically inert backbone and varied polymer architectures. However, the extent of its livingness and the underlying mechanisms of premature chain termination remain underexplored and unoptimized. In this work, we provide a functional guide to achieving exceptional molecular weight control through the systematic exploration of a model vinyl addition polymerization by (*t*-Bu_3P)-ligated cationic Pd. Using a series of chain extension experiments, we identify how the identity of the counteranion, trace impurities, and reaction conditions impact the activity and living character of the propagating species. Complementary NMR studies of a model single-insertion Pd complex afford evidence for mechanisms of chain termination through decomposition of the active catalyst. Ultimately, we demonstrate highly controlled chain extension and block co-polymerizations on the bench top with narrow dispersities, allowing for precise modulation of polymer architecture.