Modulating the Rate of Controlled Suzuki–Miyaura Catalyst-Transfer Polymerization by Boronate Tuning

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Despite the remarkable breakthroughs in catalyst-transfer polymerization (CTP) technology in the precision synthesis of conjugated polymers, modulating the monomer reactivity is still challenging. We report that, by boronate tuning, we can modulate the rate of the Suzuki–Miyaura CTP (SCTP) of 3-hexylthiophene with high control. First, cyclic boronate esters showed different polymerization rates depending on their diol subunit structure. Additionally, the rates of the *N*-coordinated boronates were differentiated by tuning their *O*- or *N*-substituents. Notably, the origin of the difference in reactivity could be explained by the N → B bond lengths. The detailed structural analysis of the resulting polymers by ^{1}H NMR and MALDI-TOF spectrometry showed that the slower and more stable boronate monomers were less prone to homocoupling and protodeboronation, thereby producing poly(3-hexylthiophene) (P3HT) with higher control (i.e., molecular weight, dispersity, end-group fidelity, and yield). By rational optimizations to suppress homocoupling and protodeboronation, well-defined P3HT were prepared at various monomer-to-initiator ratios (M/I ratios).

